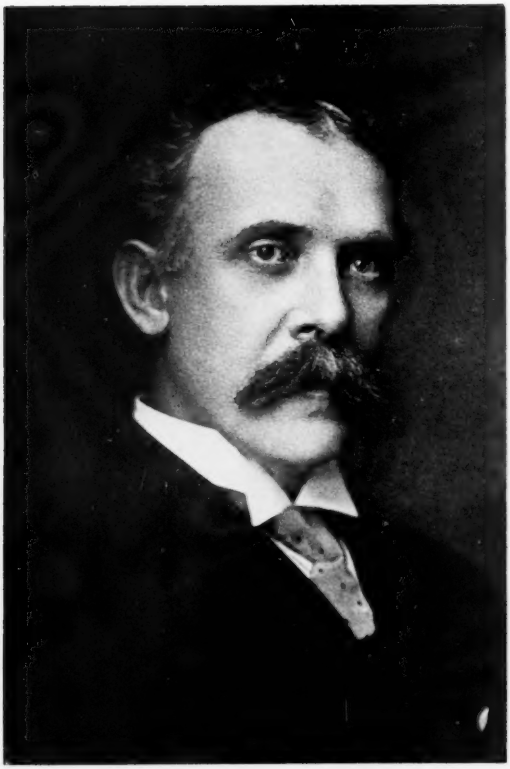

Francis P. Venable

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CHEMICAL RESEARCH IN AMERICA.[1]

BY FRANCIS P. VENABLE.

AT THE last meeting of the American Chemical Society, held in June at Buffalo, the secretary called for reports from various educational institutions as to the investigations then in progress in their laboratories. I was much struck by three things connected with these reports. The large number of institutions reporting, the wide field covered, analytical, inorganic, organic, physical, physiological, technical, and the high grade of the work. These reports promise to be one of the most interesting features of future meetings, and the thought how meagre such details would have been a decade or so ago has led me to devote this presidential address to a discussion of the progress in chemical research in America.

It is to be expected that a people, thinly scattered over a vast area of new and unbroken country, confronted with the problems and difficulties of a nation just emerging from its birth throes, would have little time to give to the arts and sciences, and yet the impetus from the wonderful discoveries of Priestley, Scheele and Cavendish and the splendid work of Lavoisier with his revolutionary deductions crossed the ocean and found its echoes in our wilderness. That Priestley, one of the greatest of these heroes of chemistry, should have been forced to flee from his native land and find refuge on these shores, and should have

[1] Presidential address delivered at the New Orleans meeting of the American Chemical Society, December 30, 1905.

continued his work here for a time, brought the great movement nearer home to us. It is a pleasure to note the appreciation of his work shown by the offer of the chair of chemistry in the University of Pennsylvania, the first institution in this country to show an active interest in the development of chemical science, and the first one to have a distinct professor of chemistry in the person of the celebrated Dr. Benjamin Rush, whose appointment dated from 1769.

This interest took active shape in the formation of the earliest known chemical societies. The Chemical Society of Philadelphia was "instituted" in 1792, forty-nine years before the founding of the London Chemical Society, the first one to be established in Europe. Its first president was Dr. James Woodhouse, professor of chemistry in the University of Pennsylvania, and Priestley was one of the members. Probably the most important paper brought before it was one by Robert Hare on the "Discovery of Means by which a Greater Concentration of Heat Might Be Obtained for Chemical Purposes." In this he announced his invention of the oxy-hydrogen blowpipe—called by him the "hydrostatic blowpipe." Hare was then only twenty years of age. Later he became professor of chemistry in the medical school of the University of Pennsylvania and had a distinguished career as an author and chemist.

In 1811 there was founded by "a number of persons desirous of cultivating chemical science and promoting the state of philosophical inquiry" the Columbian Chemical Society of Philadelphia. The patron was Thomas Jefferson, the president was James Cutbush, professor of natural philosophy, chemistry and mineralogy in St. Johns College, and the membership seems to have been drawn from a wider area, as we find among them Archibald Bruer, professor of mineralogy in Columbia College, New York; Thomas Cooper, afterwards professor of chemistry and president of South Carolina College; Edward Cutbush, professor of chemistry in Columbian University, Washington; de Butts, of the College of Maryland; Jackson, of Athens College, Ohio; Maclean, of Princeton; Silliman, of Yale; Troost, of Nashville; etc., truly a national society and the first national society with a distinguished roll of foreign members.

The Delaware Chemical and Geological Society was organized

in 1821. It was much more local in character and soon died for lack of support.

The papers presented before these societies are largely discussions of the discoveries or views of European chemists or are of a speculative character. Analyses are reported and methods of analysis devised but synthetical research is lacking. Dr. Bolton, to whom I am indebted for the foregoing facts concerning the early America nchemical societies,[1] suggests various reasons for the absence of research, but it seems to me that there is sufficient explanation in the necessity for devoting thought and strength to the development and building up of a new country and the small incentive to the search after truth for the truth's sake.

During the first quarter of the nineteenth century while European chemists were busied with atomic weight determinations, the testing of the law of multiple proportions, the extension of the list of elements and the multiplication of new compounds, the few American chemists who had access to laboratories were busied with the analysis of minerals and natural waters. It must be borne in mind that at this time there were no public laboratories either in this country or abroad to which students could readily find access. Universities did not provide laboratories for their students. Certain great teachers abroad, as Berzelius and Gay-Lussac, had private laboratories but it was extremely difficult for a young worker to secure admission. The available equipment in this country must have been meagre indeed. Even the illustration of chemical lectures by experiments was a rare thing. Liebig, in his autobiographic fragment, writes of the lectures which he heard in Paris in 1822. "The experiments were a real delight to me, for they spoke to me in a language which I understood and they united with the lectures in giving a definite connection to the mass of shapeless facts which lay mixed up in my head, without order and without arrangement." It was Liebig himself who a few years later at the University of Giessen opened to students the first public laboratory for research in chemistry.

In this country during the second and third quarters of the nineteenth century the American Journal of Science furnished an excellent medium for the publication of scientific papers. Established in 1816 by Benjamin Silliman at Yale University,

[1] This Journal, 19, 1717.

it stood for fifty years almost alone for the upbuilding of scientific investigation in America and can boast ninety years of great usefulness. Without some such journal there is little encouragement for research. The scientific man finds a keen delight in the search after truth, but he also loves to impart his discoveries to others and to win the commendation of those who can understand and appreciate his work, and there must be some arena upon which controversies can be fought out and truth winnowed from the chaff. The chemical contributions to the American Journal of Science have dealt largely with the analysis of minerals, meteorites and waters. This was especially true of the first few decades.

Schiffot Sentini[1] mentions as the first work in pure chemistry in America the formation of a compound of arsenious acid with potassium iodide. This was described in the year 1830 by J. P. Emmett. He obtained the compound in the form of a white crystalline powder by adding potassium iodide to a very dilute solution of arsenious acid, or potassium arsenite exactly neutralized with acetic acid. Emmett was professor of chemistry in the University of Virginia from its foundation in 1825 to 1842, one of the band of brilliant men brought over from England by Mr. Jefferson to aid in the upbuilding of his pet institution. With the exception of a few investigations by Robert Hare and the elder Silliman, which pertained rather to analytical, technical and mineralogical subjects, the communication of Emmett belongs to the earliest period of chemistry in North America.

It will scarcely repay us to linger over the years from 1830 to 1870. These were largely barren years. Not that chemical research was altogether lacking, but it was rather a dim and uncertain light beside the shining of such bright, particular stars as Dumas, Thénard and Marignac in France, Graham in England, Stas in Belgium, and Wöhler, Liebig and Kekulé in Germany.

One name stands out prominently during this period, conspicuous not merely because of the paucity of the work done by others but because of the sterling character of his own work. This is the name of J. Lawrence Smith. According to the elder Silliman the first piece of elaborate work or research in organic chemistry by an American was done by J. Lawrence Smith in 1842. Smith was a student of Emmett at the University of

[1] Ann. 228, 72.

Virginia, and a visit to Liebig's laboratory at Giessen formed the turning point in his life. His first organic research was entitled "The Composition of Products of Distillation of Spermaceti." In this he first made known the composition of spermaceti and set aside the views of Chevreul.

Smith was later professor of chemistry in the University of Louisiana, then in the University of Virginia and lastly in the University of Louisville where he furnished his private laboratory and did most of his work. He was an untiring worker and while much of his time was given to analyses of mineral and meteorites he was also a brilliant investigator. In analytical work we find him suggesting the use of potassium chromate for the separation of barium and strontium, and methods for the decomposition of silicates, especially the well-known method for the determination of alkalies. Only once or twice did he touch again upon organic chemistry, the subject of his first research. He contributed some sixty or seventy papers up to 1870 and his total contributions number one hundred and forty-five.

Besides the work of Lawrence Smith during this period some excellent work was done by Mallet at the University of Alabama, where he was professor of chemistry and chemist to the Geological Survey of Alabama. Here he made his first of that long and brilliant line of investigations upon the atomic weights—the first atomic weight work done in America. Following up the master work of Berzelius upon these constants, Dumas, Marignac and many others in Europe were busily engaged in making new determinations of them with all the accuracy possible from their improved apparatus and new methods. In his scantily furnished laboratory Mallet, a pupil of Wöhler, gave himself, so far as his many other duties permitted, to this exacting work, completing in 1856 his determination of the atomic weight of lithium from the chloride, and in 1859 the determination from the sulphate.

While not coming strictly under the head of researches it may be mentioned that some interesting speculations as to chemical theories were proposed by Cooke, of Harvard, and Lea, of Philadelphia, in the fifties, and we have Hinrichs' remarkable deduction of the fundamental principle of the periodic system that the properties of the chemical elements are functions of their atomic weights, drawn from the consideration of their spectra. The synoptical table of Gibbs, of Charleston, falls just beyond this

period, but is interesting to all Americans as so closely paralleling the practically cotemporaneous work of Meyer and evidently independent of it.

In this diagram, prepared for his classes in 1872, he made use of the spiral very much as was done by de Chancourtois, Meyer and Mendeléeff, anticipating in a measure the work of Spring, Reynolds and Crookes. Further he anticipated some of the geometrical work of Haughton, observing that no linear equation can be constructed to give more than rude approximations of the atomic weights, and that to construct curves, two points of inflection or contrary curvature must be given. These are the serpentine cubics afterwards worked out by Haughton.

It is not a sufficient explanation of the barrenness of this period to say that laboratories and other facilities were poor. The absence of proper facilities had not proved a bar in the way of some of the greatest chemists of the century. The spirit of investigation was lacking in our colleges and few of the teachers had the necessary training for it. Very few indeed were those who had received an inspiration by coming in contact with the great masters of the science.

A few years after the close of the great civil war American students began flocking in large numbers to the German universities. A great many of them studied chemistry under the masters of the science such as Wöhler, Liebig, Fresenius, Kekulé, and Hofmann. The best laboratories and the most enthusiastic teachers were then to be found in Germany. The marvelous development of organic chemistry offered a most attractive field of research. Very little attention was given to this branch of chemistry in America before 1875, and the facilities for investigations in organic chemistry were very limited. Such work as was done was still chiefly in the line of mineral analyses or simpler investigations among the inorganic salts. The most important work was the determination of atomic weights, and Americans may well be proud of their contributions to the knowledge of these constants which can be worthily compared with those of any nation. Cooke, Mallet, Clarke, Richards, Morley, Edgar F. Smith and others have been the leaders in this work, to which some of the best laboratories were largely given up during the last quarter of the nineteenth century.

The hundreds of young chemists, trained in the best methods of

the Germans and inspired by their contact with vigorous original thinkers, returning home, brought with them an enthusiasm and an impetus which has since placed American research well to the front. Those who had this training in the first half of the nineteenth century were comparatively few in number but they were practically the only ones who engaged in important investigations. Cooke, Mallet, Lawrence Smith and Wolcott Gibbs all studied in German laboratories.

Aside from occasional scattered papers by a student here and there the first institution to send out annual reports of researches undertaken in its laboratory was the University of Virginia. These were regularly reported by Mallet in the London Chemical News beginning with the year 1872, and have continued for thirty-three years. In 1877 the Johns Hopkins University began its work and scientific research became an essential function of every true university. From that year we may date the building up of the graduate departments of our larger, wealthier institutions and the setting into motion that immense force which is giving America its proper place among the learned nations of the world—a force which has made Germany what it is to-day. Looking back over the work accomplished it seems scarcely possible that this truly great event took place only a little more than twenty-five years ago.

In 1879 this University gave to the growing body of American chemists the first suitable journal for the publication of their researches. It is true the American Chemist, published by the Chandlers in New York, had made its appearance in 1871, but it had failed to secure the adherence and support of more than a small body of chemists and had too technical a tendency for general support. It had already passed out of existence two years before the American Chemical Journal appeared. From the beginning the distinguished editor of the latter Journal, our former president, Ira Remsen, President of Johns Hopkins University, and fully worthy of all honors which he has received, set a high standard, and for twenty-six years has maintained its excellence.

It is difficult to overestimate the influence of such a journal upon the development of research. At first the regular contributions came from a few laboratories only, notably the Johns Hopkins, Yale, Harvard, Pennsylvania, Virginia and Cincinnati.

Speedily the number grew until all parts of the country were represented and the valuable researches published placed the Journal on a plane with the best in the old world. It has thus done more to secure recognition for American research than any other one factor.

There was a crying need, however, for a strong well-organized chemical society. The memory of those early Philadelphia societies had faded out. The only common meeting ground for chemists was furnished by the sub-section of chemistry of the American Association for the Advancement of Science which did not rise, however, to the dignity of a section until 1881. It is true that this became one of the largest and most active sections of that association, gathering in annual meeting a hundred or more chemists. It is also true that certain local chemical societies were formed, but a national society was needed on the lines of the English or German or French societies. The social need for such a society for receiving and entertaining distinguished guests was especially felt during the centennial year, and so in 1876 the American Chemical Society was established in New York City. Though it failed to receive hearty support at first and the Journal appeared with discouraging irregularity and a woful paucity of pages, it grew surely and the need for it was increasingly felt. When the happy idea of local sections was evolved many of the difficulties arising from the vast territory covered by the Society disappeared, and a rapid growth ensued which has placed us in the forefront of national societies. The Journal of the Society in 1889 contained 158 pages. In 1904 the total number of pages exceeded 2300, nearly 1700 of these being taken up with original articles. The number of members of the Society is rapidly nearing the 3000 mark.

Besides the Journal of the Society and the American Chemical Journal other specialized journals have arisen and worthily represent American research. Among those may be mentioned the Journal of Physical Chemistry, the Transactions of the Electro-Chemical Society, the Chemical Engineer and others. The government scientific departments at Washington have contributed largely to the sum total of American research, and a vast amount of investigation in agricultural chemistry has been done in the laboratories of the agricultural colleges and experiment stations established in every state.

Some years ago it was humiliating to see how the work of American chemists was almost completely ignored by foreign investigators and writers. It is a source of pride to-day that we are pressing forward in every branch of pure and applied chemistry and hold a worthy place among those who are adding to the world's store of knowledge and extending the bounds of science. A distinguished European authority has lately testified to the growing strength of American research and the way in which this country is forging to the front. But the fact remains that in these hundred years and more America has produced no great chemist, no Lavoisier to develop a new chemistry, no Wöhler to break down old barriers and add a new realm to the science, no Liebig to revolutionize the agriculture and industries of a world.

In conclusion, let me plead for the encouragement of research among American chemists. I sometimes fear that the immense industrial development of the country will call away our strongest and most promising chemists to fields in which the material rewards are greater. And yet for the success of our chemical industries it is imperatively necessary that a large army of quiet workers should be busied in investigation, in the simple search after truths without a dream of the practical utilization of the results obtained. These are the men who patiently and laboriously forge the chain, link by link, that leads to some of the greatest economic changes, often changing the industries of a whole nation. It is chiefly in the laboratories of our colleges and universities that these investigators must be found. There alone can the necessary freedom of purpose, of view and of action be preserved. There alone is the truth all important and the money value unconsidered. No truth is insignificant, no fact is too trifling to warrant observation and careful accounting. It was in the laboratory of the University of Giessen that Liebig did his quiet work that made agriculture a science and made possible much of the comfort and luxury of the present day. It was Graebe and his discovery of synthetic alizarin in the laboratory of the University of Berlin which revealed the value of the almost useless coal tar and laid the foundations of Germany's great commercial growth. And many lesser cases might be cited. The governments of Europe vie with one another in fostering chemical research, Germany most wisely doing this in

her universities. We as a nation cannot long afford to be behind them in this matter. In the close competition of the near future we must depend upon these toilers of the laboratories for our supremacy in the world's markets. But to my mind a far stronger plea for investigation lies in the inspiration which comes from such work, the broadening horizon and the fuller life.

What are the conditions necessary for chemical research and can we meet these conditions in most or all of our educational institutions? As the spirit of research seems to have developed with the increase in wealth of our larger institutions, many have come to regard research as a prerogative of these institutions and expensive equipment as a prerequisite to it. The idea is totally false and calculated to do much harm. It is accepted by many who hold positions in the smaller colleges as an excuse for their quietly sinking into a dull round of routine and unproductive drudgery. I do not believe that any teacher of science can keep fresh and enthusiastic and have a touch of inspiration about him unless he keeps in touch with nature through personal investigation of her facts and laws. And unless a teacher has these qualities he is not worth his salt and should not have the opportunity for dulling the originality of others. It too often happens that our young chemists, having completed their researches at some of the larger institutions, published their dissertations, won their doctorates and secured professorships in minor colleges, stifle their consciences with the excuse that they lack equipment or leisure, give up all idea of original work, settle down to a humdrum teaching of text-books and limit their ambition to drawing their meagre salaries and grumbling at their poor opportunities.

Let me tell you that which is no secret but is open to every one who has studied the history of the science, neither fine laboratory nor costly outfit nor abundant leisure are essentials for the search after nature's secrets. These are good and helpful things but the one essential is the earnest investigating mind, enthusiastic, determined and plucky in surmounting obstacles. A quiet corner, a little apparatus, some spare time snatched from a multitude of other duties, these will suffice to give any one the opportunity to show what is in him. If he fails to avail himself of it, it is a tacit confession to his lack of energy, or originality, or pluck. He need not grumble at his meagre salary. He is getting more than he is worth.

I do not mean to be unjust or harsh but when I think of the thousands of young men who year after year are subjected to deadening, uninspiring, humdrum teaching of science and are thus lost to the ranks of our workers, and of the possible brilliant, elect spirits among that number, I must cry out at the terrible waste. The field of knowledge is vast and growing vaster with the ever-widening horizon. The harvest is plentiful and the call for laborers is ever more insistent. It is necessary to impress this great truth that the true teacher must be a learner also, drawing constantly fresh inspiration from the fountain head.

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 8.]

CONCERNING SILVER OXIDE AND SILVER SUBOXIDE.

BY GILBERT NEWTON LEWIS.

Received December 18, 1905.

ON account of the uncertainty as to the correctness of the value at present accepted for the electrolytic potential of oxygen, I have attempted to calculate this extremely important quantity by an indirect method. One of the important data needed in this calculation is the decomposition pressure of silver oxide at 25°. The determination of this pressure is the subject of the present paper. Incidentally it will be necessary to consider the question of the existence of the silver suboxide, which has been described by certain chemists.

LeChatelier[1] was the first to show the reversibility of the reaction,

$$2Ag_2O = 4Ag + O_2.$$

By the decomposition of silver oxide in a closed tube at 300° he obtained a pressure of 10 atmospheres. On the other hand, by heating silver at the same temperature in oxygen at 15 atmospheres he observed the oxidation of the silver. He therefore placed the decomposition pressure of silver oxide between 10 and 15 atmospheres.

Knowing this pressure for one temperature, and the heat of decomposition, it should be possible to calculate with the aid of the van't Hoff equation, the pressure at another temperature. Such a calculation, however, must be made with great caution.

[1] Z. physik. Chem. 1, 516 (1887).

It is especially important to make sure that at both temperatures we are dealing with precisely the same reaction.

Now Guntz[1] has undertaken to show that the pressure that he obtained by heating silver oxide in a closed tube at 358° was not the decomposition pressure of silver oxide but of silver suboxide. In other words he believed that the silver oxide decomposed first entirely into suboxide and oxygen according to the equation

$$4Ag_2O = 2Ag_4O + O_2,$$

and that the suboxide then partially decomposed until equilibrium was reached, according to the reaction,

$$2Ag_4O = 8Ag + O_2.$$

The existence of such a suboxide would not prevent the determination of the equilibrium pressure in the system Ag, Ag_2O, O_2, for this pressure could be readily calculated from the pressure of equilibrium in the system Ag_2O, Ag_4O, O_2 and that in the system Ag_4O, Ag, O_2.

I shall, however, show that in my experiments over a wide range of temperature silver suboxide never appeared, and that the experiments which led M. Guntz to believe in its existence must probably be interpreted otherwise.

I shall first describe measurements of the decomposition pressures obtained by heating silver oxide at several different temperatures, and then undertake to show that the pressures obtained are the true pressures of equilibrium in the system Ag_2O, Ag, O_2.

Two samples of silver oxide were used in these experiments. They will be referred to as A and B. A was prepared with the exclusion of carbon dioxide from hot dilute barium hydroxide and silver nitrate as described in my paper on the kinetics of the decomposition of silver oxide.[2] B was the preparation of Merck, labeled "highest purity." Both samples before being used were heated for several hours at 300°.

DECOMPOSITION PRESSURE OF SILVER OXIDE AT 325°.

The first experiment was made at 325°[3] in the thermostat of molten sodium and potassium nitrates which I have previously

[1] C. R. 128, 996 (1899).

[2] Z. physik. Chem. 52, 310 (1905).

[3] All thermometers used were compared with Reichsanstalt standards. The corrected temperatures are given.

described.[1] The apparatus for measuring the pressure consisted of a stout brass tube, about 2 meters in length and 1 cm. in internal diameter, closed at the lower end, and at the upper connected with a metallic manometer. In the lower end of the brass tube was fitted a thin glass tube, 7 cm. high, containing the silver oxide (sample B). In order to diminish as far as possible the total air space in the apparatus the rest of the brass tube was filled as nearly as possible with a close fitting glass rod. After the apparatus had been exhausted through a stop-cock provided for that purpose, the lower end of the tube was introduced into the thermostat to a depth of about 30 cm.

The decomposition began in a few hours, and in five days the pressure reached a constant maximum as shown in Table I.

TABLE I.

Time in hours.	Pressure in atmospheres.
12	18.5
24	26.5
48	29.8
72	30.1
96	31.5
120	31.8
144	31.8

In order to approach the equilibrium from the other side the tube was then heated to a higher temperature for a few hours and returned to the thermostat. The pressure had risen to 34 atmospheres but gradually fell as shown in Table II.

TABLE II.

Time in hours.	Pressure in atmospheres.
0	34.0
24	33.4
48	32.5
72	32.3

It is apparent therefore that the pressure of equilibrium lies between 31.8 and 32.3 atmospheres. The manometer had been verified by comparison with a standard manometer, but may nevertheless have been in error by about half an atmosphere. We will take therefore in round numbers 32 atmospheres as the decomposition pressure at 325°.

During this whole experiment there was not the slightest leakage from the tube and the whole apparatus proved to be

[1] Loc. cit.

eminently satisfactory. Unfortunately the work was interrupted at this point by my removal to another laboratory and the experiments had to be continued with new and simpler apparatus.

EXPERIMENTS AT 302°.

The next experiments were made in a bath of diphenylamine vapor. The first method tried was an indirect one. It consisted in heating the silver oxide in a closed glass tube, drawn out at one end to a capillary, cooling it suddenly by removal from the bath, opening the capillary under a gas burette and calculating from the volume of gas evolved and from the volume of the tube (exclusive of that occupied by the remaining mixture of silver and oxide) the pressure that had been exerted in the tube at the temperature of the bath.

Eight tubes containing different quantities of silver oxide were suspended in the vapor of boiling diphenylamine in a large iron receptacle, and kept there for six days. During this time it was found necessary to renew the diphenylamine several times on account of its gradual decomposition. The original substance (Kahlbaum's) boiled at 302°. In the course of the experiment several of the tubes were broken; in others the oxide was entirely decomposed, so that finally only one of the eight tubes could be used for determining the pressure. This was broken under water and 8.58 cc. (760 mm. 30°) of oxygen collected in the burette. The tube was weighed, then filled with ether, boiled to drive out all the air, refilled, and weighed. From these two weighings the volume of the tube was found to be 0.92 cc. The pressure at 302° must therefore have been $\frac{8.58+0.92}{0.92} \times \frac{273+302}{273+30}$, or 18.0 atmospheres. We shall show presently that this value is too small. The oxide used was sample A which decomposes far more slowly than B, and it is probable that equilibrium had not been reached when the tube was removed from the bath.

On account of the difficulty of determining when the reaction had come to equilibrium this indirect method was abandoned and the following adopted.

Two tubes, one having a bore of 1 mm., the other of 3 mm. were joined together and then drawn apart at the junction so as to form a fine capillary about 1½ meters long (BCD in Fig. 1). In the

smaller tube, D, a short column of mercury was introduced and the open end sealed, thus making an ordinary closed manometer which could be calibrated in the usual way at the end of the experiment. The tube B was filled with silver oxide and sealed at the open end.

The large bath used in the previous experiment had also to be abandoned on account of its large consumption of diphenylamine, of which only a limited supply was available. A simpler bath made of a long-necked glass boiling flask was found to answer the purpose satisfactorily. The neck was about 2 cm. in diameter and was insulated on the outside by a jacket of asbestos. The temperature of the vapor in different parts of the neck was frequently tested. The variations over a considerable range rarely exceeded one-half a degree if contact with the walls was avoided. The tube B was therefore held in the neck by a simple framework which prevented its touching the walls.

In a previous paper I have shown that the decomposition of silver oxide is extremely slow until a large amount of silver has already formed, which acts as a catalyzer. Therefore in order to hasten the attainment of equilibrium the tube containing the silver oxide was heated at the beginning to a higher temperature than that of the bath until a part of the oxide was decomposed. It was then introduced into the bath and heated continuously, except that at the end of each twenty-four hours it was removed and the diphenylamine renewed. After being returned to the bath the pressure always assumed immediately its value previous to the removal of the tube, thus showing that during the rapid cooling and heating the reaction did not proceed to any appreciable extent.

During the experiment the temperature varied between 301.5° and 303°. We may take 302° as the average temperature. (One degree change of temperature causes a change of less than half an atmosphere in the decomposition pressure.)

The first experiment was made with sample B of oxide. After being enclosed in the tube it was heated gently with a Bunsen burner until small flecks of metallic silver appeared throughout the mass. It was then introduced into the bath, the manometer indicating a pressure of 6 atmospheres. At the end of two days the pressure had reached 16.7 atmospheres and was increasing very slowly. The tube was then removed from the bath and

heated until a little more of the oxide was decomposed. When replaced in the bath the manometer registered 20.2 atmospheres and during the next twenty-four hours this pressure remained constant within one-tenth atmosphere. The tube was again removed and heated until on being replaced in the bath the pressure was 23.2 atmospheres. In the next twenty-four hours this fell to 21.6 atmospheres and in twenty-four hours more to 21.5 atmospheres.

This experiment shows that the decomposition pressure at 302° must be greater than 16.7 (contrary to the conclusions of LeChatelier), is probably not far from 20.2 and is certainly not greater than 21.5 atmospheres.

The experiment was then repeated with another tube containing the same kind of oxide. In this case a longer time was allowed for equilibrium to become established. Table III shows the pressure at the end of each twenty-four hours.

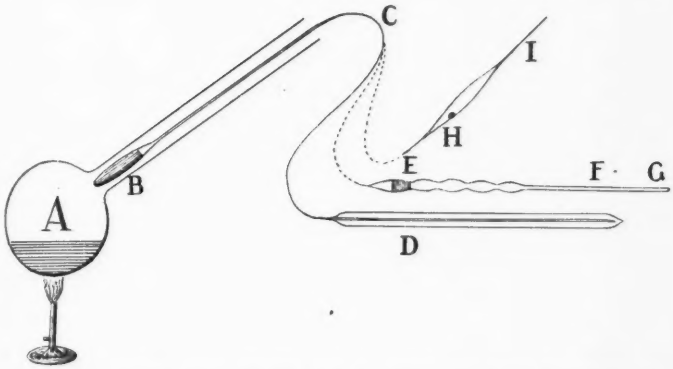
TABLE III.

Time in days.	Pressure in atmospheres.
1	11.1
2	15.1
3	17.3
4	18.8
5	19.5
6	19.7
7	19.7
8	19.7

It is evident from these two experiments that the true value for the pressure at 302° must lie between 19.7 and 21.5 atmospheres, and probably nearer the lower figure. Let us take 20.5 atmospheres as a value sufficiently exact for our purpose.

EXPERIMENTS AT 445°.

The next experiments were made at the temperature of boiling sulphur, the bath being constructed as in the last experiment. At this temperature also the first attempts were made with an indirect method. The simple method tried at 325° was not attempted here, as it seemed probable that the tube could not be cooled rapidly enough from this high temperature to prevent a displacement of equilibrium. Instead, the following method was tried. The construction of the apparatus is indicated in Fig. 1 (BCHI). A thick-walled glass tube, of not more than 2 mm.



internal diameter, was drawn out to form the long capillary C. The tube B, on one side of this capillary, was filled with silver oxide and sealed at the free end. The other tube was again drawn out to a capillary at I and sealed, leaving 3 or 4 cm. between H and I. During this construction a small piece of tar was placed loosely in the tube, where it narrowed to a capillary at H.

When the tube had been in the bath long enough for equilibrium to be established, a hot glass rod was brought for a moment in contact with the tube at H, thus melting the tar and causing it to run into the capillary. This heating was purely local and had no appreciable effect on the temperature of the gas in the tube HI.

After the tar had solidified the capillary was broken at C, leaving in the tube HI the same pressure that had existed in B. The capillary I could then be opened under water and the pressure calculated from the volume of gas evolved and the volume of the tube HI.

While this method was being used experiments were also made with a direct method, and a manometer was finally constructed which gave very satisfactory results.

The tube BCEFG was drawn from a single tube of the same sort used in the preceding method. At E it was drawn out into a series of small bulbs, as these proved to be stronger than a simple straight tube, and it finally terminated in a long capillary which had a nearly uniform bore (about 0.1 mm.) in the region

FG. The pressure was registered by a small mercury column, starting originally at E when at atmospheric pressure, and moving to a point F, about 10 cm. from the end of the capillary, when the pressure reached its maximum. On breaking the tube at C after the experiment the mercury invariably returned to its original position at E. The point G was then broken off within 0.1 or 0.2 mm. of the end and the volumes FG and EG determined by drawing in mercury successively to F and to E and weighing the mercury. The smaller quantity which weighed only a few milligrams was weighed on a fine assay balance. I believe that this manometer should give accurate results. The error caused by the capillarity of the mercury is not over 0.1 atmosphere, nor is it likely that the change in volume of the capillary tube under pressure would lead to any considerable error.

There were two difficulties in both the methods that I have described. At the high pressure of over 200 atmospheres which was here reached the glass tubes would explode on the slightest provocation. Fortunately, although explosions in the outer tubes were frequent, the tube B within the bath rarely gave way. This difference in behavior between two tubes of the same form, drawn from the same piece of glass is undoubtedly to be attributed to the annealing and toughening of the tube B resulting from the high temperature. The danger of explosion was reduced as far as possible by choosing flawless tubes and drawing them as carefully as possible. The fine capillaries never burst and probably could have withstood a much higher pressure than that to which they were subjected.

The other difficulty was that ordinarily enough silver oxide could not be packed into the tube B to give the pressure of equilibrium before being entirely decomposed. This difficulty was overcome by filling only one-half of the tube B with silver oxide, the other half with dry, powdered potassium permanganate, which decomposes instantaneously at the temperature of the bath and produces much more oxygen than the same volume of silver oxide. The two substances were separated by a small piece of asbestos.

Experiments in which the manometer was used showed that equilibrium was reached in from fifteen to forty minutes, according to the kind of oxide used. In one case an addition was

made to the apparatus in an extra bulb at C, filled with potassium permanganate. After the manometer had come to rest as usual, the bulb C was gently heated causing a further increase of pressure. But this excess of pressure rapidly diminished through the re-oxidation of the silver in B and within less than ten minutes the manometer showed the original pressure, within a small fraction of an atmosphere, thus proving that we are dealing with a true equilibrium.

The first experiments with both methods gave disappointing results. Under similar circumstances the results obtained by the two methods were in full agreement (after allowing for the difference in compressibility[1] of the air and oxygen contained respectively in the tubes EG and HI), but the results obtained at different times ranged from 175 to 200 atmospheres. A more careful investigation of the temperature in the neck of the boiling flask pointed to the cause of the variations. A preliminary test had appeared to show the temperature to be the same in the neck and the body of the flask, but it was now found that the temperature in the former was subject to variations, depending upon a number of conditions, such as the angle at which the flask is held, the height of the heating flame, and other more or less adventitious circumstances. This difference between the sulphur and diphenylamine baths is probably not due so much to the higher temperature of the former as to the great viscosity of the liquid sulphur which condenses in the neck of the flask. The silver oxide had been put in the neck rather than the body of the flask in order to avoid possible changes in temperature due to spattering of superheated liquid. But this superheating was now proved to be small. A Reichsanstalt standard thermometer showed the temperature of the liquid to vary under varying conditions between 445° and 446°, that in the vapor immediately above, between 443.5° and 444.5°. Since the thermometer may have been in error by 1° or 2° (it was calibrated at 397° and at 505°) we will use for the temperature of the vapor in the body of the flask, where the tube B was placed in the following experiments, the commonly accepted value for the boiling-point of sulphur, namely 445°.

Four new experiments were now made, all by the second

[1] Amagat : Ann. Chim. [5] 19, 345 (1880); [5] 22, 353 (1881).

method, with the manometer. For illustration I will give the details of the first of these experiments.

The mercury column which moved rapidly at first towards the end of the manometer gradually came to rest as equilibrium was reached. The positions of this column (distance from end of manometer) at intervals of about five minutes are given in Table IV. The experiment was begun at 10.25 o'clock.

TABLE IV.

Distance in mm.	Time.
65.0	10.32
53.9	10.35
49.0	10.40
45.9	10.45
45.5	10.50
45.2	10.55
45.2	11.00
45.2	11.05
45.3	11.10
45.2	11.15
45.2	11.25

The capillary at C was then broken and the manometer calibrated. 0.842 gram of mercury filled the whole manometer, 0.00413 gram filled it to the point, 45.2 mm. from the end, where the mercury column came to rest. If we assume Boyle's law, the pressure was therefore $\frac{0.842}{0.00413}$ or 204 atmospheres.

The results of this and three other similar experiments are given in Table V.

TABLE V.

No. of experiment.	Kind of oxide.	Pressure.
1	B	204
2	B	191
3	B	200
4	A	205

Experiment 2 differed from the others in that the silver oxide was almost entirely used up. The result is undoubtedly too low. Discarding this value therefore and taking the average of the other three the result is 203 atmospheres.

The preceding calculations have been based on the assumption that the air in the manometer obeys Boyle's law. According to the work of Amagat[1] the true pressure of air in the neighbor-

[1] Loc. cit.

hood of 200 atmospheres is, at 0°, about 2½ per cent. higher than that calculated from the volume by Boyle's law. At 30°, the temperature of the manometer, this correction would be somewhat less, say 2 per cent. Making this correction, therefore, we get 207 atmospheres as the equilibrium pressure of silver oxide at 445°.

DOES SILVER SUBOXIDE EXIST?

M. Guntz[1] heated silver oxide to a temperature of 358° for fifty hours and obtained a pressure of 49 atmospheres. This he considered the pressure of equilibrium in the reaction

$$2Ag_4O = 8Ag + O_2$$

and cited as evidence for this view the following experiment: In a closed tube were placed known weights of silver and silver oxide and a quantity of potassium permanganate sufficient to yield enough oxygen to produce a pressure higher than 49 atmospheres at 358°. The whole was heated at this temperature for three days. The tube was then cooled rapidly and it was found that the silver had gained in weight and the silver oxide had lost in weight by amounts which indicated the formation of Ag_4O in both cases.

I shall show presently that in all my experiments carried on at temperatures from 300° to 445°, and with two different samples of silver oxide, the suboxide of silver was never formed. It seems difficult to reconcile my results with those of M. Guntz. Of course it is conceivable that the suboxide is capable of existence and that it appeared for some reason in one case and not in the other, just as occasionally some hydrate may be suddenly precipitated from an aqueous solution, although it may fail to appear many times under apparently similar circumstances. But I am inclined to believe that the experiments of M. Guntz can be explained without the necessity of assuming the existence of the suboxide. If the pressure in the tube that he used was greater than the decomposition pressure of silver oxide the gain in weight of the silver can be readily explained by its oxidation to silver oxide. The loss in weight of the silver oxide can only be explained by assuming that it contained water or carbon dioxide. I should consider this improbable if it were not for the fact that my own experiments have shown how difficult it is to prepare

[1] Loc. cit.

and to keep silver oxide free from these impurities. It is perhaps not generally known that carbon dioxide, as well as water, is rapidly taken up by silver oxide from the atmosphere. One sample which I prepared in such a way that it was very free from impurity absorbed a large quantity of carbon dioxide while standing for a month in a loosely corked bottle. When carbon dioxide and water are once present they can be expelled only with great difficulty. Some of the former frequently remains after the silver oxide has been heated for an hour or two at 300°.

That silver suboxide was not present in any of the experiments that I have described will be evident from the following considerations. According to the phase rule silver, silver oxide, silver suboxide, and oxygen could not all exist together in equilibrium. In the absence of suboxide only one state of equilibrium is possible, that between Ag, Ag_2O, O_2. But in case the suboxide could form, two states of equilibrium would be possible, namely between Ag_2O, Ag_4O, O_2, and between Ag_4O, Ag, O_2. With a given quantity of silver oxide enclosed in a small volume the first equilibrium would exist, in a larger volume, the second.

In all the experiments previously described the final mixture in the tube has contained silver, as shown by the color, and by the metallic flakes produced upon grinding the whole in a mortar. In any given case, therefore, the remaining black powder must be a single phase, either all silver oxide or all silver suboxide. Let us assume that it is the latter and see to what consequences we are led. For example, let us assume that the pressure of 32 atmospheres which we obtained at 325° is the decomposition pressure of silver suboxide. Now suppose that we enclose so much silver oxide in a tube that if it should all decompose according to the reaction

$$4Ag_2O = 2Ag_4O + O_2,$$

a pressure of over 32 atmospheres would result. Then metallic silver could not form and the only possible equilibrium would be that between the oxide and suboxide.

This very experiment was tried. A glass tube was filled with silver oxide, sealed, and heated for a week at 325°. At the end of this time a considerable quantity of silver had formed, although, calculated from the volume of the tube and the amount of oxide, over 100 atmospheres would have been generated by the change from the oxide to the suboxide alone. A similar

experiment was made at 345°. A small quantity of silver was placed in a tube and covered with a little glass wool. The rest of the tube was filled as full as possible with silver oxide. The tube was then sealed and left in the thermostat for five days, at the end of which time not only was the silver unoxidized but white spots of silver had appeared throughout the oxide.

These experiments show pretty conclusively the absence of silver suboxide. A still stronger proof is given by the experiments at 302°. In one of the experiments at this temperature which showed the pressure of equilibrium to be about 20 atmospheres, the volume of the tube and the manometer and the weight of silver oxide were determined. It was found that enough oxide had been used to produce a pressure of 35 to 40 atmospheres, if it had all changed merely to suboxide, yet a considerable quantity of silver was found in the final mixture.

Finally it was found possible to show by direct analysis that the black powder left in the tubes was not silver suboxide. It sometimes happened that at the end of the experiment the silver oxide was almost entirely decomposed in one part of the tube and apparently unchanged in another. This was due to the fact that the decomposition, being autocatalytic in character, progresses very rapidly at any point where it has once begun. In one experiment at 302° a considerable portion of the black substance left in the tube appeared to contain no silver. A sample of this weighing 0.0892 gram was heated in a tube connected with a gas burette. It yielded 4.71 cc. of oxygen (at 27°, 760 mm.). The above quantity of pure silver oxide should give theoretically 4.73 cc. This is an unexpectedly good agreement.

In the experiments at 445° there was no case in which the remaining oxide did not contain some silver, but two samples were chosen which appeared to be least decomposed. 0.205 gram of the first gave 7.24 cc. of oxygen (calculated for Ag_2O, 10.85 cc.; for Ag_4O, 5.42 cc.). 0.0851 gram of the second gave 4.35 cc. (calculated for Ag_2O, 4.52 cc.; for Ag_4O, 2.26 cc.). It is obvious that here also the black substance cannot be silver suboxide and is presumably silver oxide mixed with a certain amount of silver.

THE HEAT OF FORMATION OF SILVER OXIDE.

We have now obtained the pressure of equilibrium at different temperatures between silver, oxygen, and a certain black powder.

We have proved that this black powder is not silver suboxide but that at 302° and, presumably at the other temperatures as well, it has exactly the composition, Ag_2O. There still remains the possibility that this substance, although of the same composition as the silver oxide which exists at ordinary temperatures, may be an allotropic phase. In other words there may be a transition temperature, between room temperature and the temperatures of our experiments, at which a break in continuity in the properties of silver oxide occurs. This possibility must be eliminated before we can safely calculate the decomposition pressure of silver oxide at 25° from the pressures at the higher temperatures.

In order to decide whether we are dealing with the same phase of silver oxide at high and low temperatures, we will determine from the change in the decomposition pressure between 302° and 445° the heat of decomposition of the silver oxide occurring at these temperatures, and compare this value with the one obtained at ordinary temperatures by other methods.

The heat of decomposition may be found from the change of pressure with the temperature, by the aid of the equation of van't Hoff, which in this case has the form

$$\frac{d\ln p}{dT} = \frac{Q}{RT^2} \qquad (1)$$

where p is the decomposition pressure, T the absolute temperature, R the gas constant, and Q the heat absorbed when 1 gram-molecule of oxygen is formed according to the equation

$$2Ag_2O = 4Ag + O_2.$$

This equation of van't Hoff is not strictly exact but is derived with the aid of two assumptions from the equation of Clausius,

$$\frac{dp}{dT} = \frac{Q}{T(v - V)} \qquad (2)$$

where v is the molecular volume of oxygen at the temperature T and at the pressure p, and V is the total change of volume of the solid system, that is, it is the volume of 2 gram-molecules of silver oxide less that of 4 gram-molecules of silver. Q is the heat absorbed during the decomposition. It may be replaced by the expression, $U + p(v - V)$, where U is the increase in internal energy accompanying the decomposition, and $p(v - V)$ is the work done. In the integration of the van't Hoff equation U is

usually regarded as constant, but since we are dealing with a pretty wide range of temperature we shall obtain a more accurate result by regarding it as a linear function of the temperature according to the equation

$$U = U_o - CT \tag{3}$$

where C is the diminution in the heat capacity of the system during the decomposition of 2 gram-molecules of silver oxide. We may therefore write in place of equation 2,

$$\frac{dp}{dT} = \frac{U_o - CT + p(v - V)}{T(v - V)} \tag{4}$$

In order to obtain equation 1 from equation 2 or 4, it is necessary to make two assumptions: First, that the oxygen obeys the gas law, and second, that the volume V is negligible compared with v. Since the deviation of oxygen from the gas law is small at ordinary temperatures[1] and is undoubtedly much smaller at the temperature of our experiments, the first assumption will not lead to any appreciable error. The second assumption would also be justifiable, if it were not for the fact that in our experiments at 445° the pressure is so great and consequently the volume v so small that in comparison V cannot be neglected.

Regarding V not as a negligible but as a constant quantity, and assuming that $pv = RT$, I have succeeded in obtaining the integrated form of equation 4,

$$ln \frac{p_1}{p_2} = -\frac{U_o}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) + \frac{V}{R}\left(\frac{p_1}{T_1} - \frac{p_2}{T_2}\right) + \frac{R - C}{R} ln \frac{T_1^2}{T_2} \tag{5}$$

With the aid of this equation we are able to calculate from the decomposition pressures at any two temperatures the value of U_0. In order to do this we must know the values of V and C, but the terms in which these quantities occur are comparatively unimportant ones in the equation, and both these quantities can be disregarded altogether without very seriously influencing the result. Their approximate values will therefore suffice.

From the tables of Landolt and Börnstein we find for the densities of silver and silver oxide 10.5 and 7.5 respectively.

[1] Amagat: Loc. cit.

[2] This equation may be readily verified by differentiating it. The resulting equation by suitable transposition and with the aid of the gas law can be readily shown to be identical with equation 4. Equation 5 may be obtained by an independent method from equations 6 and 7 of my paper entitled "Law of Physico-Chemical Change." Z. physik. Chem. 38, 205 (1901).

Calculating from these the molecular volumes we get approximately 20 cc. as the value of V.

The specific heat of silver oxide has not been determined but the value of C may be found from the principle of the constancy of the atomic heat in solids. The heat capacity of silver is doubtless approximately the same in the oxide and in the metal. C therefore is the difference between the heat capacity of oxygen in the gaseous and solid states. The heat capacity at constant volume of 32 grams of oxygen in the gaseous state is 5 (calories per degree). The heat capacity in the solid state is about 8,[1] whence C equals 3.

We will determine the value of U_0 in calories and therefore use for R the value 2.0, except in the next to the last term of equation 5, in which, if the pressure is expressed in atmospheres and the volume in cubic centimeters, R must be expressed in corresponding units and given the value 83.

We have three sets of experimental values (*a*) $T=445+273$, $p=207$; (*b*) $T=302+273$, $p=20.5$; (*c*) $T=325+273$, $p=32$. These may be used in equation 5 in pairs. Using values (*a*) and (*b*) we find for the first term of the equation, $ln\frac{p_1}{p_2}$, the value 2.31; for the third term, 0.06; for the fourth term,—0.11. Combining these we get for the second term the value 2.36, whence U_0 is 13600 small calories.

Using similarly values (*a*) and (*c*) we find for U_0 the same value, 13600.

From values (*b*) and (*c*) we find, $U_0=13300$. This value is to be given less credit on account of the nearness of the two temperatures used.

The remarkably good agreement between these values shows conclusively that we are dealing with the same reaction throughout the whole range of temperature from 302° to 445°. As the final result we will take $U_0=13600$ small calories or 136 K (Ostwald calories). From equation 3 the value of U at room temperatures is therefore 128 K. This is the increase of internal energy accompanying the decomposition of 2 gram-molecules of silver oxide. The heat of formation of silver oxide at room temperatures, exclusive of external work, is therefore one-half this value or 64 K.

[1] See for example Ostwald's Lehrbuch.

HEAT OF FORMATION OF SILVER OXIDE, OTHERWISE DETERMINED.

For the heat of formation of silver oxide we find in the literature only two determinations which are at all trustworthy. Thomsen[1] allowed copper to act upon silver nitrate and from the heat of this reaction, the heat of formation of copper nitrate, and the heat of neutralization of silver oxide, calculated the heat of formation of the latter to be 59 K (*a*).

Berthelot[2] by a similar method obtained 70 K (*b*).[3]

In his experiments on the energetics of galvanic elements Jahn[4] obtained the following equation:

$$Pb + 2AgNO_3Aq = Pb(NO_3)_2Aq + 2Ag + 509K.$$

Let us combine this equation with the following:

$$PbO + 2HNO_3Aq = Pb(NO_3)_2Aq + H_2O + 178K \text{ (Thomsen)},$$

$$Pb + O = PbO + 503K \text{ (Thomsen)},$$

$$Ag_2O + 2HNO_3Aq = H_2O + 2AgNO_3Aq + 104K,[5]$$

whence,

$$2Ag + O = Ag_2O + 68K \quad (c).$$

A similar calculation can be made as follows: I have measured the electromotive force of the following cell (see following paper),

$$Hg,\ HgCl,\ KCl^{N}/_{10},\ KNO_3{}^{N}/_{10},\ AgNO_3{}^{N}/_{10},\ Ag,$$

and found it to be 0.393 volt at 30°. The temperature coefficient is —0.00121 volt per degree.

From these figures we find by the Helmholtz equation,

$$Hg + \overline{Cl} + \dot{Ag} = Ag + HgCl + 176K$$

with this we will combine the following,

$$\tfrac{1}{2}Ag_2O + \dot{H} = \dot{Ag} + \tfrac{1}{2}H_2O + 52K,$$

[1] Not having Thomsen's book at hand, the values here attributed to him are taken from Ostwald's Lehrbuch.

[2] Ann. chim. **15**, 186 (1878).

[3] All these values are for the "total" heats of reaction. I have chosen to use these values, which include the external work, since they are the ones commonly given in the literature. The reduction to the simple "internal" heat of reaction will be made later.

[4] Wied. Ann. **28**, 493 (1886).

[5] Thomsen gives 54 K, but Berthelot found 52 K by the neutralization of silver oxide with nitric acid, Ann. Chim. [5] **4**, 188 (1875), and also by its precipitation with alkalies, Ibid. [5] **4**, 503 (1875), and has recently verified this value by new experiments, C. R. **133**, 555 (1901).

$$HgCl + Cl = HgCl_2 + 219K.^1$$
$$Hg + 2Cl = HgCl_2 + 533K.^2$$
$$Cl + \tfrac{1}{2}H_2O = \overset{-}{Cl} + \overset{+}{H} + \tfrac{1}{2}O + 50K.^3$$

Hence,

$$2Ag + O = Ag_2O + 72K \quad (d).$$

Recently Jouniaux[4] has determined the conditions of equilibrium at several temperatures between silver, hydrochloric acid gas, silver chloride and hydrogen, and has thus obtained the thermochemical equation,

$$Ag + HCl = AgCl + H + 71K.^5$$

Let us combine with this equation the following equations of Berthelot:

$$HCl + Aq = \overset{+}{H} + \overset{-}{Cl} + 174K,$$
$$\overset{+}{Ag} + \overset{-}{Cl} = AgCl + Aq + 157K,$$
$$\tfrac{1}{2}Ag_2O + \overset{+}{H} = \overset{+}{Ag} + \tfrac{1}{2}H_2O + 52K,$$
$$H + \tfrac{1}{2}O = \tfrac{1}{2}H_2O + 345K,$$

whence

$$2Ag + O = Ag_2O + 66K.$$

If instead of using the equations of Berthelot we use those of Thomsen[6] we get a different value, namely 60 K. The average of these is 63 K (*e*).

We have thus found five independent values of the heat of formation of silver oxide, varying from 59 K to 72 K. These values all include the external work. In order to obtain the mere change of internal energy, 3 K must be subtracted from each of the above numbers. We have then, (*a*) 56; (*b*) 67; (*c*) 65; (*d*) 69; (*e*) 60.

[1] This value was obtained by Thomsen from the direct action of chlorine upon calomel. It is in all probability correct, as it has not been called into question in the critical work on mercury salts of Nernst, Z. physik. Chem. **2**, 23 (1888), and Varet, C. R. **120**, 620 and 921 (1893).

[2] This value was obtained independently by both Nernst and Varet.

[3] Thomsen's value is 50.5 K (Pogg. Ann. **148**, 177–1873), Berthelot's is 48 K (C. R. **109**, 546 and 590 (1889)). Thomsen's value is probably the more accurate.

[4] C. R. **132**, 1270 (1903).

[5] I have added 3 K to the value given by Jouniaux in order to obtain the "total" heat of reaction.

[6] Except the third (see a previous note).

Not one of these values alone can be regarded as reliable, on account of the uncertainty in the various data used, but they are all obtained from perfectly independent data, the only value entering into all being the heat of solution of silver oxide in acid, and this has been reliably determined. We may therefore regard the average of these figures with a good deal of confidence. This average is 63.4 K and is very close to the value (64 K) obtained in the preceding section. This very satisfactory agreement proves conclusively that the silver oxide which exists between 302° and 445° is, from a thermodynamic point of view, identical with that which exists at ordinary temperature.

DECOMPOSITION PRESSURE OF SILVER OXIDE AT 25°.

We are now able to calculate from equation 5 the equilibrium pressure between silver oxide, silver, and oxygen at 25°. For data we will take 20.5 atmospheres as the pressure at 302°; 64 K as the heat of formation of silver oxide at 25°; and for C the value 3, as before. The third term of the equation containing V, may be here neglected. We thus obtain $p_{25} = 5 \times 10^{-4}$.

When we consider the question of how much this value is affected by possible errors in the data used, we find that errors in p_{302} and in C have much less influence than an error in U_{25}. An error of 1 K in the latter would cause an error of about one unit in the significant figure of p_{25}. We may therefore regard this value as almost certainly correct within two units.

In the following paper I shall show that from this value of the decomposition pressure of silver oxide at 25° it is possible to calculate the electrolytic potential of oxygen, and that the value thus obtained differs very widely from the one at present accepted.

SUMMARY.

The equilibrium pressures in the system, silver oxide, silver, oxygen, at the temperatures 302°, 325°, and 445°, are respectively 20.5, 32, and 207 atmospheres.

It has been proved that silver suboxide was absent in all of the experiments and that probably it is incapable of existence, at least at these temperatures.

From the change of equilibrium pressure with the temperature the heat of formation of silver oxide is found to be 64 K (Ostwald calories).

The mean of five determinations of this quantity based on calorimetric data is between 63 K and 64 K.

The decomposition pressure of silver oxide at 25° is calculated to be 5×10^{-4} atmospheres.

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 9.]

THE POTENTIAL OF THE OXYGEN ELECTRODE.

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THERE are no more essential physico-chemical data than the changes of free energy accompanying those important chemical processes in which oxygen takes part. Many of these free energy changes could be calculated directly if the potential of the oxygen electrode, against a given concentration of hydroxyl ion, were accurately known. The purpose of the present paper is to determine the true value of this potential.

An oxygen electrode was first used by Grove in the cell which bears his name. The electromotive force of this cell, which is composed essentially of an oxygen and a hydrogen electrode dipping into an aqueous solution, has been measured by a number of experimentors.[1] The value most frequently met in the literature is 1.07–1.08 volts, as found by Smale,[2] who was the first to show that the electromotive force of such a cell is independent of the nature of the electrolyte used.

This value of 1.07–1.08 volts was generally accepted as the true electromotive force of the oxygen-hydrogen cell, or in other words, the true measure of the free energy of formation of water from its elements, but was later shown to be probably too low, by the work of Bose,[3] Wilsmore[4] and Czepinski,[5] who found that the electromotive force of an oxygen-hydrogen cell in normal sulphuric acid increases after several days' standing to 1.10–1.12 volts.

Assuming that between the substances present in the cell there is no reaction possible which can produce a greater change

[1] See bibliography by Bose: Z. physik. Chem. 34, 730 (1900).

[2] Z. physik. Chem. 14, 577 (1894).

[3] Loc. cit.

[4] Z. physik. Chem. 35, 291 (1900).

[5] Z. anorg. Chem. 30, 1 (1902).

of free energy than is associated with the union of oxygen and hydrogen to form water, then we must assume that the true potential of the oxygen-hydrogen cell is at least as high as the highest value obtained, namely 1.12 volts. This is in fact the value most generally adopted at present.

Westhaver,[1] however, apparently considers the above assumption incorrect when platinum electrodes are used, and prefers to take for the electromotive force 1.06 volts, which he obtains by means of an iridium electrode.

Bose,[2] taking 1.12 volts as only the lower limit of the electromotive force, has tried to find also its upper limit. He concludes that the electromotive force must lie between 1.12 and 1.15 and probably lies nearer the lower value. The method which he used for obtaining the upper limit seems, however, to be quite erroneous. It consisted in increasing the electromotive force artificially by depositing oxygen electrically upon the oxygen electrode, and in noting the lowest point to which the electromotive force then sank after the lapse of considerable time. Bose assumed that this value must be higher than the true electromotive force of the cell, but this assumption is certainly not true. Westhaver found that after charging similarly the iridium electrode with oxygen, the electromotive force fell in a few days to 1.06, the normal value, and even to a lower value, 0.9 volt when the electrode was completely immersed. According to Bose's view the latter figure would have to be taken for the upper limit of the electromotive force, and this is obviously absurd.

A number of other cases might be cited to show that the principle is erroneous. For example, I may mention the following experiment: To a solution of cobaltous sulphate, ammonium sulphate and ammonium hydroxide are added. The mixture shaken with air absorbs a large quantity of oxygen. If it is then immediately acidified it becomes a very powerful oxidizing agent and rapidly evolves oxygen. A platinum electrode dipped into this solution is immediately covered with bubbles of oxygen, but its (oxidizing) potential is several tenths of a volt less than that which an ordinary oxygen electrode would have in a solution of the same acidity.

The only upper limit to the electromotive force of the oxygen-

[1] Z. physik. Chem. **51**, 65 (1905).

[2] Z. Elektrochem. **7**, 673 (1901); Z. anorg. Chem. **30**, 406 (1902).

hydrogen cell which we can obtain from existing data is the lowest electromotive force at which it is possible to electrolyze water and produce definitely recognizable bubbles of oxygen and hydrogen. According to Coehn and Osaka[1] this value is 1.28 volts.

Granting then that the true electromotive force lies between 1.12 and 1.28 volts, what reason have we for believing that the lower of these two values is any more nearly correct than the higher? The belief that the electromotive force actually measured with ordinary oxygen and hydrogen electrodes is the true reversible electromotive force of the oxygen-hydrogen cell is based on two assumptions which are unsupported by any experimental evidence. The first of these assumptions is that when a small current flows through the cell (a current of such magnitude as is used in electromotive force determinations) the accompanying reaction is simply the formation of water from its elements. The second assumption is that this reaction occurs in a perfectly reversible way.

As far as the hydrogen electrode is concerned there is no question but that both assumptions are correct. Hydrogen passes quantitatively and reversibly into hydrogen ion. But it is very doubtful if at the other electrode oxygen passes just as smoothly into oxygen or hydroxyl ion. Richarz and Lonnes[2] studied the products formed when water, in the presence of air, was electrolyzed between electrodes of polished platinum. The conditions of the cathode when a current is passing through this cell are nearly identical with the conditions at the oxygen electrode when it is made the cathode. In both cases hydrogen would be deposited on the electrode if it were not for the presence there of oxygen. In both cases in place of the deposition of hydrogen oxygen goes into electrolytic solution. The only difference in the two cases is that in one the electrode is of platinized platinum, bubbled over with oxygen; in the other the electrode is of polished platinum in contact with dissolved air. Now in their experiments Richarz and Lonnes found that as the dissolved oxygen was consumed at the cathode, not water, but hydrogen peroxide was formed in nearly equivalent amount. Thus with a current density of about 2×10^{-7} amperes per square centimeter, passing for five

[1] Z. anorg. Chem. 34, 86 (1903).

[2] Z. physik. Chem. 20, 145 (1896).

obtained 88 per cent. of the theoretical yield of peroxide, and even more than this had probably formed and in part decomposed before the analysis.

Since the conditions at the cathode in this experiment are not identical with those at the oxygen electrode, we cannot conclude necessarily that the reactions going on when a current passes are the same in both cases, but the conditions are so similar that we are at least led to consider the possibility that the main reaction in the oxygen-hydrogen cell is the union of oxygen and hydrogen, not primarily to form water, but to form hydrogen peroxide. If this is the case, the observed electromotive force is the measure of the free energy of formation of hydrogen peroxide, and since this is smaller (even bearing in mind that the peroxide is kept at a low concentration by the presence of the platinum black) than the free energy of formation of water, the electromotive force corresponding to the latter reaction would be considerably higher than the one actually observed.

This assumption is far from improbable. We know indeed that in other cases when oxygen takes part in chemical reactions at ordinary temperatures, it almost invariably enters into combination first as the radical (O_2), forming substances of the type of peroxides.

There is, moreover, another more specific argument in favor of this assumption. It has frequently been observed[1] that upon the addition of hydrogen peroxide to the liquid about the oxygen electrode, the electromotive force of the oxygen-hydrogen cell instead of increasing, as was expected, diminishes. There have been several ingenious attempts to explain this phenomenon, but they are entirely unnecessary if we assume that hydrogen peroxide is formed by the reaction of the cell, for it is a familiar principle that the electromotive force of any cell is lowered by increasing the concentration of any of the products of the electrolytic reaction.

But supposing that in spite of all these facts we assume that the reaction in the cell is simply the formation of water; even then the assumption that this reaction occurs reversibly is quite improbable in view of the slowness of almost all processes of

[1] See, for example, Glaser: Z. Elektrochem. 4, 374 (1898); Wilsmore: Loc. cit.

oxidation at ordinary temperatures, even in the presence of platinum black.

In this discussion I have attempted to show only that we have at present no satisfactory evidence that the true electromotive force of the oxygen-hydrogen cell may not be much higher than any of the values hitherto obtained by direct measurement. If it is in fact higher, the question is how we are to obtain its true value. Three methods suggest themselves.

If all chemical reactions occurred instantaneously, every galvanic cell would always give the highest possible electromotive force. In other words, of all the reactions possible in the cell, that one evolving the most free energy would alone occur and occur reversibly. It is the slowness of some essential part of the process which causes the condition of irreversibility. One method, therefore, of approaching the true electromotive force of a cell which ordinarily acts irreversibly is to introduce some substance which catalyzes the electrolytic reaction. In our present problem this method would consist in finding for the oxygen electrode some more powerful catalyzer than platinum black.

The second method is based on the principle that when at a given electrode two distinct electrochemical reactions can take place, corresponding to two different potentials, a reaction will tend to occur between the substances concerned, of such a sort as to equalize the two potentials. Thus a platinum electrode dipping into a solution of ferric and ferrous salts has a definite potential. If we introduce a small quantity of potassium iodide at the electrode, iodine will be set free until the potential between iodine and iodine ion is equal to that between the ferric and ferrous ions. So if at the oxygen electrode an oxidizable substance, say a chloride, is added, we should expect chlorine to be set free until the potential between chlorine and chlorine ion equals the true potential between oxygen and the hydroxyl ion at its given concentration. In other words from a strong, slow oxidizing agent an equally strong, but rapid, oxidizing agent may be formed.[1] The reaction may, however, be too slow for the method to be practicable, unless a suitable catalyzer is present.

[1] Spencer and Abegg, Z. anorg. Chem. **44**, 379 (1905), have made application of this principle in determining the electromotive force of the oxygen-hydrogen cell and obtained 1.14 volts, but by a method which appears to me erroneous.

I have made a number of attempts to apply this principle, using various substances such as manganese, cobalt and cerium salts which are known to catalyze the process of autoxidation, but these experiments are still incomplete and their discussion may be postponed.

I may point out in this connection that a phenomenon observed by Wilsmore[1] is probably an illustration of the principle we are considering. He found that the electromotive force of the oxygen-hydrogen cell in normal sulphuric acid is at first 1.08 volts, but rises in the course of a few days to 1.12 volts. The sulphuric acid in the neighborhood of the oxygen electrode then showed on analysis the presence of some oxidizing agent. When it was replaced by fresh acid the electromotive force returned at once to 1.08 volts. Apparently from the sulphuric acid, or from an impurity, the oxygen produced some substance which was a more active, although of course not a more powerful, oxidizing agent than itself.

Both of these methods for determining the true electromotive force are rendered difficult by the extreme slowness which characterizes reactions at ordinary temperatures in which oxygen takes part. The third method, which is the one I have employed, consists in determining at a higher temperature the free energy of some reaction into which oxygen enters, and thus calculating from suitable data the free energy of the same reaction at ordinary temperatures, and the potential of the oxygen electrode.[2] Three reactions appeared especially suitable for this purpose, (1) the decomposition of silver oxide, (2) the decomposition of mercuric oxide, (3) the reaction between oxygen and hydrochloric acid gas (Deacon process). The first of these promised to give the most accurate results and was chosen first for study.

In the paper immediately preceding I have discussed carefully the conditions of equilibrium in the system, $2Ag_2O = 4Ag + O_2$, and have shown that at 25° silver oxide and silver are together in equilibrium with oxygen if the latter has a pressure of 5×10^{-4} atmospheres. I showed that this value is probably not in error

[1] Loc. cit.

[2] An ingenious attempt of this sort has been made by Preuner, Z. physik. Chem. 42, 50 (1903), who made use of the equilibria between carbon, oxygen and hydrogen, at high temperatures. He obtained 1.15 volts for the oxygen-hydrogen cell but unfortunately the experimental data are too inaccurate to permit a very reliable calculation of this kind.

by more than one, almost certainly not by more than two units in the significant figure.

From the fundamental laws of energy it is obvious therefore that a galvanic cell at 25° composed of a silver electrode, a saturated solution of silver oxide and an oxygen electrode must have zero electromotive force when the pressure of the oxygen is 5×10^{-4} atmospheres.

It is easy to calculate what electromotive force the same cell will have at the same temperature when the oxygen is at atmospheric pressure. The equation is obviously

$$E = \frac{0.0590}{4} \log \frac{1}{5 \times 10^{-4}}$$

where E stands for electromotive force, log for common logarithm and 0.0590 is the familiar constant occurring in all equations for the electromotive force of a concentration cell at 25°.

Hence we may write,

Ag, Ag_2O(sat.), O_2(1 atmosphere); $E = +0.049$ volt.[1] (1)

Granting that our value for the decomposition pressure of silver oxide is not in error by more than two units at the most, we must regard the above value of E as accurate within 2 or 3 millivolts.

The concentration of the ions in a saturated solution of silver oxide has been determined in a number of independent ways by Whitney and Melcher,[2] by Noyes and Kohr,[3] by Abegg and Cox,[4] and by Böttger.[5] Of these determinations, which are in fairly good agreement with one another, that of Böttger is the only one that was determined by a direct method and is, I believe, the most accurate. He obtained, by measuring the electrical conductivity, the value 1.39×10^{-4} for the equivalent concentration of the ions in saturated silver oxide at 25°. In his work all the customary precautions were taken, and moreover an analysis of the results shows them to be mutually consistent.

[1] All the following values will be for 25° unless the contrary is stated. We will in general call E positive when the positive current tends to pass within the cell from the first electrode to the second. E will be given exclusive of any potentials between the electrolytes of the cell, unless otherwise stated.

[2] This Journal, **25**, 69 (1903).

[3] Z. physik. Chem. **42**, 336 (1902).

[4] Ibid. **46**, 1 (1903).

[5] Ibid. **46**, 521 (1903).

Thus for example from the solubility that he gives for silver oxide at 25° and at 20°, I have calculated the heat of solution of silver oxide and obtained a value only a few per cent. different from that obtained calorimetrically.

Noyes and Kohr determined accurately the ratio between the concentrations of silver ion in saturated silver oxide and in saturated silver chloride, and found it to be almost exactly ten. From this value and from the solubility of silver chloride given by Kohlrausch and Rose[1] they obtain 1.5×10^{-4} as the ion concentration in saturated silver oxide.

Using instead of the value of Kohlrausch and Rose the ones obtained through electromotive force measurements by Goodwin[2] and by Thiel,[3] we find 1.25×10^{-4} and 1.4×10^{-4} respectively.

Here, in the case of silver chloride also, I believe that the best determination is that of Böttger. He determined the solubility of silver chloride at 19.95° to be 1.06×10^{-5}. From the known heat of solution of silver chloride I calculate that at 25° this value would become 1.31×10^{-5}. Hence for silver oxide we have 1.3×10^{-4}.

All these determinations show that the value directly obtained by Böttger, 1.4×10^{-4}, can hardly be in error by more than a few per cent. If it were in error by 20 per cent., it would cause an error of one centivolt in our final value for the potential of oxygen.

We may now write in place of equation (1),

$$\mathrm{Ag},\ \mathrm{Ag}^{+}(1.4\times10^{-4}\text{ normal}),\ \mathrm{O\overline{H}}(1.4\times10^{-4}\text{ normal}),\ \mathrm{O}_2\ (1\text{ atmosphere});\ \mathrm{E}=+0.049\text{ volt.} \qquad (2)$$

Using now the familiar Nernst equation we may write,

$$\mathrm{Ag},\ \mathrm{Ag}^{+}(1.4\times10^{-4}n),\ \mathrm{Ag}^{+}\frac{n}{1},\ \mathrm{Ag};\ \mathrm{E}=+0.0590\log\frac{1}{1.4\times10^{-4}}=+0.227\text{ volt,} \qquad (3)$$

and

$$\mathrm{O}_2(1\text{ atmosphere}),\ \mathrm{O\overline{H}}\ (1.4\times10^{-4}n),\ \mathrm{O\overline{H}}\ \frac{n}{1},\ \mathrm{O}_2\ (1\text{ atmosphere});\ \mathrm{E}=-0.227\text{ volt.} \qquad (4)$$

Combining (2), (3) and (4),

$$\mathrm{Ag},\ \mathrm{Ag}^{+}\frac{n}{1},\ \mathrm{O\overline{H}}\ \frac{n}{1},\ \mathrm{O}_2(1\text{ atmosphere});\ \mathrm{E}=-0.405\text{ volt.} \qquad (5)$$

[1] Z. physik. Chem. **12**, 242 (1893).
[2] Ibid. **13**, 577 (1894).
[3] Inaug. Diss., Giessen (1900).

It is obvious that we are now in a position to determine immediately the potential of oxygen against a normal solution of hydroxyl ion, knowing that between silver and a normal solution of silver ion. As no particularly reliable investigation of the latter potential has been made I have determined it anew.

It has been pointed out by Richards and Lewis[1] that satisfactory results for the potentials of solid metals can best be obtained by using the metals in a finely divided state. The employment of this method in the present case has the important advantage that we may use for the silver electrode the very same sort of silver as occurs in the equilibrium upon which our calculations are based. The electrodes were made as follows. A platinum wire was sealed into a glass tube and the projecting part wound into a small spiral. This spiral was inserted in a tube containing silver oxide and the whole was heated at 445° until all the oxide was decomposed. The electrode was then removed from the tube and consisted of a platinum spiral completely enclosed in a loosely cohering mass of finely divided silver. Six of these electrodes were made from two different samples of silver oxide (see preceding paper). For the purpose of comparison five electrodes were also made of the type recommended by Goodwin,[2] consisting of silver foil electroplated with silver.

The individual electrodes were placed in a decinormal solution of silver nitrate in separate vessels of the type commonly used for single electrodes, so that they could be compared either with a standard electrode or with each other.[3] As soon as measurements were begun it became apparent that, although the electrodes of each class did not agree entirely among themselves, there was a much wider difference between the two classes. The average potential of the plated electrodes differed by about one-hundredth of a volt from the average potential of the new type of electrodes, the plated electrodes being more negative.[4] As

[1] Z. physik. Chem. **28**, 1 (1899).

[2] Loc. cit.

[3] The following measurements were all made in a thermostat at 30°. As the work was done in the tropics it was difficult to maintain a lower temperature than this.

[4] It was interesting to note that two electrodes plated like the others but with such a large current that the silver came down, not in a smooth film, but in a kind of sponge, gave a potential nearly equal to that of the finely divided silver.

the potentials were measured at intervals for more than a month and this difference persisted throughout, there can be no doubt that the potentials of the two kinds of silver are really different.

In regard to constancy and agreement among themselves the advantage lay with the new electrodes. The six electrodes frequently showed differences between the extremes of 4 or 5 millivolts, but the average deviation from the mean was not over 1 millivolt. Moreover, these electrodes underwent no sudden changes of potential such as the plated electrodes were subject to. They fluctuated in value, but slowly and gradually. The potential of a single electrode would ordinarily change only a few tenths of a millivolt in a day. One of these electrodes was compared with a standard electrode soon after being set up and again after nearly six months. During this time it had changed 2 millivolts.

As standard electrodes I used two decinormal calomel electrodes which were made up at different times out of entirely different materials. They differed from one another by less than 0.2 millivolt.

The cells measured were of the type,

$$Ag,\ AgNO_3\ n/10,\ KNO_3\ n/10,\ KCl\ n/10,\ HgCl.$$

The average electromotive force obtained at 30° with the several finely divided silver electrodes was —0.393 volt, which may be in error by 1 or possibly 2 millivolts. This value includes the potentials between the electrolytes which amount to nearly 2 millivolts. Exclusive of these potentials the electromotive force is therefore —0.391 volt.

I determined the temperature coefficient of this electromotive force between 30° and 0° and found it to be 0.00121 volt per degree, the numerical value of the electromotive force diminishing with increasing temperature. For 25° we have therefore,

$$Ag,\ AgNO_3\ n/10,\ D.\ E.\ (decinormal\ electrode);\quad E=-0.397\ volt. \tag{6}$$

For the difference in potential between the decinormal and normal electrodes we will take,[1]

$$D.\ E.,\ N.\ E.;\ E=-0.054\ volt. \tag{7}$$

Now assuming that decinormal silver nitrate is 81 per cent. dissociated[2] we find,

[1] See Ostwald-Luther: Phys. Chem. Messungen.

[2] This is the value given by Kohlrausch for 18°. Rudolphi has shown that the degree of dissociation in this case is nearly independent of the temperature: Z. physik. Chem. 17, 385 (1895).

$$Ag, \overset{+}{Ag}\ n/1, AgNO_3\ n/10, Ag; E=-0.064 \text{ volt.} \quad (8)$$

Combining (6), (7) and (8),

$$Ag, \overset{+}{Ag}\ n/1, \text{N. E.}; E=-0.515 \text{ volt.} \quad (9)$$

The true electrolytic potential of silver against normal silver ion is therefore —0.515 volt if we take that of the normal electrode as zero, or —1.079 volts if we give to the latter, as is conventional, the potential —0.560 at 18° or —0.564 at 25°.

Combining now (5) and (9) we find,

$$O_2 \text{ (1 atmosphere)}, \overset{-}{OH}\ n/1, \text{N. E.}; E=-0.110 \text{ volt.} \quad (10)$$

This value, —0.110 volt, is therefore the true potential between oxygen at atmospheric pressure and a normal solution of hydroxyl ion, if the potential of the normal electrode is zero. If the latter is taken as —0.564 volt, we have —0.674 volt for the "absolute" electrolytic potential of oxygen, a value which is probably not in error by more than a few millivolts, and certainly not by more than 1 centivolt unless we have entirely overlooked some possible source of error.

We can also express this potential in terms of the hydrogen potential. Wilsmore[1] has shown that,

$$H_2 \text{ (1 atmosphere)}, \overset{+}{H}\ n/1, \text{N. E.}; E=+0.283 \text{ volt.} \quad (11)$$

Hence from (10)

$$O_2 \text{ (1 atmosphere)}, \overset{-}{OH}\ n/1, \overset{+}{H}\ n/1, H_2 \text{ (1 atmosphere)}; E=-0.393 \text{ volt.} \quad (12)$$

From this value it is now possible to calculate the true electromotive force of the ordinary oxygen-hydrogen cell if we know the concentration of the hydrogen and hydroxyl ions in pure water. We will take for this concentration at 25° the value 1.05×10^{-7}, calculated from the conductivity measurements of Kohlrausch and Heydweiller.[2] This value, as is well-known, has been corroborated by several independent methods so that it is in all probability accurate to within 10 per cent. If it were in error by as much as 20 per cent. an error of 1 centivolt would be caused in our final result.

The concentration of hydroxyl ions in a solution normal with respect to hydrogen ion is $(1.05\times10^{-7})^2$ or 1.1×10^{-14}.

[1] Z. physik. Chem. 35, 291 (1900).

[2] Ibid. 14, 317 (1894).

Therefore,

O_2 (1 atmosphere), $\overline{OH}$ $n/1$, $\overset{+}{H}$ $n/1$, O_2 (1 atmosphere); E = +0.824 volt. (13)

From (12) and (13),

H_2 (1 atmosphere), $\overset{+}{H}$ $n/1$, O_2 (1 atmosphere); E = +1.217 volts. (14)

This, our final value for the electromotive force of the hydrogen-oxygen cell, is a tenth of a volt higher than the highest value ever obtained by direct measurement. It is quite improbable that it is in error by more than 1 centivolt. Its accuracy depends essentially upon the accuracy of three data, (1) the decomposition pressure at 25° of silver oxide, (2) the solubility of silver oxide, (3) the electrolytic dissociation of water.

It is important finally to determine the temperature coefficient of the potential of the oxygen electrode. I will indicate briefly the essential steps in this calculation.

We have found,

Ag, $AgNO_3$ $n/10$, D. E.; E = —0.397 + 0.00121 (t—25°). (15)

Now Richards[1] has accurately determined the temperature coefficient of the decinormal electrode and found it to be 0.00079 volt per degree. If we take the "absolute" potential of this electrode at 25° as —0.618 volt (N. E. at 25° = —0.564), then at any other temperature it has the value, —0.618—0.00079 (t—25°).

Combining this value with equation (15) we have for the electrode Ag, $AgNO_3$ $n/10$ the potential —1.015 + 0.00042 (t—25°).

From the theory of concentration cells, we have

Ag, $\overset{+}{Ag}$ $n/1$, $AgNO_3$ $n/10$, Ag; E = —0.064—0.00021 (t—25°).

Whence the potential of Ag, $\overset{+}{Ag}$ $n/1$ is —1.079 + 0.00021 (t—25°).

According to equation (5)

Ag, $\overset{+}{Ag}$ $n/1$, $\overline{OH}$ $n/1$, O_2 (1 atmosphere); E = —0.405 volt.

We can determine by the Helmholtz equation the temperature coefficient of this electromotive force, from the electromotive force itself, and from the heat evolved in the reaction of the cell, which is the heat of formation of silver oxide plus its heat of solution. This amounts, according to the preceding paper, to

[1] Z. physik. Chem. **24**, 39 (1897).

—53 Ostwald calories per gram-equivalent. Using this value in our calculations we find,

$$E = -0.405 - 0.00058\ (t - 25°).$$

Combining this value with that for the single potential of Ag, $\overset{+}{Ag}$ $n/1$ given above, we find for the "absolute" potential, O_2 (1 atmosphere), $\overline{OH}$ $n/1$, the value $-0.674 + 0.00079\ (t - 25°)$.

The work described in this and in the preceding paper was begun in the Chemical Laboratory of Harvard College, but was carried out for the most part in the Government Laboratory in Manila. It is now being continued in the Research Laboratory of Physical Chemistry of the Massachusetts Institute of Technology, where I am investigating the free energy change connected with the action of oxygen on hydrochloric acid gas. In this way I hope to make another independent determination of the potential of oxygen.

SUMMARY.

A consideration of the known facts concerning the potential of the oxygen electrode shows that there is good ground for believing that the present accepted values for the electromotive force of the oxygen-hydrogen cell may all be much too low.

A new form of silver electrode is described and its potential measured.

From this potential, the decomposition pressure of silver oxide, and the solubility of silver oxide, the true potential at 25° of an oxygen electrode against normal hydroxyl ion is found to be —0.674 volt (the normal electrode at 18° being taken as —0.560 volt).

From this value and from the electrolytic dissociation of water the true electromotive force at 25° of the oxygen-hydrogen cell is calculated to be 1.217 volts, a value which is probably correct within less than 1 centivolt.

The temperature coefficient of the oxygen electrode is also calculated.

NOTE.

The last number of the Zeitschrift für Elektrochemie contains a statement by Professor Nernst, to the Bunsen Gesellschaft, that he has calculated the electromotive force of the oxygen-hydrogen cell from the dissociation of water vapor, and obtained

the value 1.23 volts, a value very close to the one found in this paper. A comparison of the two methods will be interesting in order to determine which is better capable of giving the most accurate results.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CINCINNATI, NO. 68.]

SOME NOTES ON TRIVALENT COBALT AND NICKEL.

BY STANLEY R. BENEDICT.

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IN view of the recent work of Tubandt[1] and Barbiere and Calyolari,[2] describing the formation of trivalent compounds of nickel and cobalt by electrolysis, it has been thought advisable to publish the following paper, preliminary in nature, describing results obtained which indicate more or less conclusively the existence of certain compounds of cobalt and nickel hitherto unprepared. Because of the instability of these compounds, very few have as yet been isolated. In all the instances herein described, however, the reactions given by the solutions seem to the writer to demonstrate the existence of the supposed, or closely allied, compounds. Hence it may not be entirely out of place to publish these partially worked out laboratory notes.

In a previous paper[3] the writer described a method for the detection of nickel which depends upon the formation of cobaltioxalic acid, salts of which had previously been made by both Kehrmann[4] and Marshall,[5] though not in the same way as that described by the writer. It was also mentioned in that paper that by a process analogous to the one described, other new compounds had been made which would be described later. An outline of this work and its continuation follows.

Cobaltioxalic acid may be obtained in solution as follows: A solution of a cobalt salt is treated with a slight excess of sodium peroxide and heated to boiling. The black cobaltic hydroxide thus obtained is filtered off and washed on the filter with hot water a few times, and then with ice water until completely

[1] Z. anorg. Chem. **45**, 73 (1905).

[2] Atti. Accad. Lincei Roma, 5, **14**, I, 464. Chem. Centralbl, 1905, **1**, 464.

[3] This Journal, **26**, 695 (1905).

[4] Ber. **19**, 3101.

[5] J. Chem. Soc. **59**, 760 (1891).

cooled to the temperature of this wash-water. A cold, saturated solution of oxalic acid is now poured repeatedly through the filter. A considerable portion of the cobaltic hydroxide dissolves, yielding a green solution which closely resembles solutions of nickelous salts in color. This solution may very readily be shown to contain trivalent cobalt by treatment with sodium hydroxide and warming, when a black precipitate of cobaltic hydroxide will be obtained.

It exhibits the following properties: Upon standing a few hours a spontaneous reduction takes place, the color changing from green to pink, accompanied by a precipitation of cobaltous oxalate. Heating to boiling causes a reduction, though by no means an instantaneous one, it often being necessary to continue the boiling several minutes to effect complete reduction. The reduction in the cold is only slightly accelerated by the presence of sulphurous acid or hydrogen sulphide. This indifference to reducing agents is surprisingly great, and is even more marked in presence of excess of sodium carbonate solution. Solutions made alkaline with sodium carbonate are not noticeably reduced by boiling (though they cannot be evaporated to dryness without reduction), and appear to be unaffected by ferrous salts and even by stannous chloride. The formula of this acid, deduced from its salt described below is, $H_6Co_2(C_2O_4)_6$.

The calcium salt of cobaltioxalic acid may be obtained pure as follows. The acid solution prepared as described above is treated with an excess of pure calcium carbonate and the solution agitated until a neutral or only faintly acid reaction (due to carbonic acid) is obtained. The solution is now filtered off from the excess of carbonate and calcium oxalate. The filtrate contains now (theoretically) only calcium cobaltioxalate, together with some carbonic acid. This solution should yield no precipitate with calcium chloride solution in the cold, but will deposit calcium oxalate upon boiling. It is evaporated to dryness in a vacuum desiccator at ordinary temperature and the salt thus obtained recrystallized from water. As thus prepared, the calcium salt is in the form of dark green needles, crystallizing with six molecules of water. A quantitative determination gave Ca 13.50, C_2O_4 60.20, and H_2O 12.08 per cent., showing conclusively that its composition corresponds exactly with the barium salt pre-

pared by Kehrmann,[1] which he found to have the following formula $Ba_3Co_2(C_2O_4)_6.6H_2O$.

A solution of this calcium salt exhibits great stability regarding reducing agents, none of those tried, among which were hydrogen sulphide, ferrous sulphate, sulphurous acid, and stannous chloride, reducing it in the cold. If silver nitrate solution be added to a solution of calcium cobaltioxalate, a white precipitate slowly forms, the solution still retaining its green color, showing that the cobalt is still trivalent. The precipitate is found upon examination to be silver oxalate. The filtrate will give no precipitate upon boiling with calcium, showing that all the oxalate has been removed. The question naturally arises as to what form the cobalt is in after removal of the oxalate. It would appear to have to be either a simple or complex cobaltic nitrate. This point is to be further investigated.

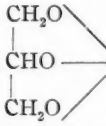
A more rapid method for the preparation of potassium cobaltioxalate than the one described by either Kehrmann[1] or Marshall,[2] is the following: To a neutral solution of cobalt nitrate an excess of solid potassium oxalate is added and the solution warmed. A heavy precipitate of cobalt oxalate forms at first but soon dissolves in the excess of potassium oxalate forming a deep red solution. A little sodium carbonate solution is now added (no precipitation takes place) then bromine water is added and the solution warmed to boiling. Practically all of the cobalt present is converted into the cobaltioxalate compound, coloring the solution a deep greenish black, which, upon considerable dilution, yields a solution nickel-green in color. The black solution is treated with excess of solid calcium hydroxide with constant stirring until all excess of oxalate has been removed. The solution is now filtered and the filtrate treated with a slight excess of alcohol. This precipitates the green potassium cobaltioxalate which may be filtered off and recrystallized from water. Kehrmann[1] gives a description of its properties.

If a solution of a cobalt salt be treated with some glycerol, then a little sodium hydroxide and next some bromine water be added and the solution boiled, a black solution is obtained which contains a trivalent compound of cobalt. This compound may be isolated by precipitating with a mixture of equal parts of

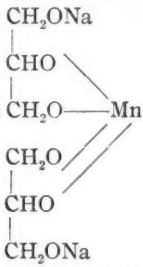
[1] Kehrmann: Loc. cit.

[2] Marshall: Loc. cit.

alcohol and ether, and washing off the excess of glycerol with alcohol. As thus obtained the compound is a black, amorphous substance, soluble in water to a black solution. No attempt has yet been made to crystallize this substance from its aqueous solution nor to analyze it. For this reason its formula can only be suggested. Certain indications point to the following compound of trivalent cobalt with glycerol,



These indications are (1) we are certain that we have not a simple cobaltic nitrate or hydroxide, (2) if we substitute manganese for the cobalt in the above reaction, a deep red solution is obtained, corresponding in its properties to a solution of a manganic-glycerol compound described by Schottlander,[1] who ascribed to it the formula



We can substitute tartrate for glycerol in the reaction described for cobalt above, obtaining in this case a black compound less stable and more difficult of isolation than the glycerol compound.

The impossibility of obtaining compounds containing trivalent nickel, other than the hydroxide, has been set forth in the text-books as one of the few distinctions in the behavior of nickel and cobalt. Recently however, Tubandt[2] has prepared a compound of trivalent nickel by electrolysis. It will be shown below that we can readily obtain solutions of nickelic salts without recourse to electrolysis.

To prepare a solution of nickelic acetate the procedure is as follows: Freshly precipitated nickelic hydroxide is filtered off and washed upon the filter first with hot water, then with ice

[1] Ann. 155, 230 (1870).

[2] Tubandt: Loc. cit.

water until entirely cooled to the temperature of this wash-water. A 90 per cent. solution of acetic acid which has been previously cooled to just above its freezing-point is now poured upon the filter. The first portion of the filtrate will be green in color and contain practically no trivalent nickel. (This is probably due to the heat liberated by the reaction of the acid with the excess of alkali always present.) In a moment however the nickelic hydroxide will dissolve with little or no reduction, yielding a filtrate coal-black in appearance which gives the reactions we should expect of trivalent nickel. All reducing agents cause immediate reduction, the solution changing from black to green in color. Reduction takes place shortly upon standing and instantaneously upon warming. Sodium hydroxide solution gives an immediate precipitate of black nickelic hydroxide.

Strong solutions of tartaric or citric acid may be substituted for acetic acid in the above, the solutions thus prepared resembling that obtained with acetic, save that they are slightly less stable. They all liberate iodine from potassium iodide with instantaneous reduction, but have little, if any, similar action upon potassium bromide.

Attention is called to the slight differences in the mode of procedure given above and that usually employed for obtaining a solution of cobaltic acetate in acetic acid. In the latter case the reaction is carried on in a test-tube at ordinary temperatures, under which conditions a considerable amount of trivalent cobalt is obtained in solution, but this procedure will yield absolutely no trivalent nickel compound. Hence it has been stated that such a compound cannot be obtained. Yet if we substitute a filter for a test-tube and use cold solutions, the desired product is readily obtained. It is a fact that the trivalent hydroxides of both cobalt and nickel dissolve from a filter with less reduction than they do in a test-tube. If an attempt is made to prepare the cobaltioxalic acid described earlier in this paper by shaking cobaltic hydroxide with oxalic acid, in a test-tube, it will be found that little or none at all will be formed, whereas if cobaltic hydroxide be treated on a filter with oxalic acid, a considerable amount of the compound is readily obtained. Unless we suppose that the oxygen in the air and pores of the filter aids in preventing reduction, this fact appears very difficult of explanation.

If for the cold acetic acid solution used in obtaining a solution of nickelic acetate as described above, we substitute a nearly saturated solution of bisulphate of potassium, a very interesting result is obtained. (*Note.*—The bisulphate solution should not be cooled much, or too much of the salt is deposited.) The first portion of the filtrate is (as with the acetic acid) green in color. In a later portion this color is less apparent until soon a filtrate is obtained which is practically colorless. Yet this filtrate contains a large amount of nickel, as can readily be shown by adding sodium hydroxide solution to it. As more of the bisulphate solution filters through (pouring more upon the filter if necessary), the filtrate again becomes colored, but now the color is pink instead of green. The pink color is faint at first, but gradually increases in depth until in most instances a distinctly reddish pink solution is obtained. This solution upon standing deposits a green, crystalline salt and becomes more deeply colored. There is little or no doubt that from the time the filtrate comes through colorless it contains trivalent nickel, apparently nickelic sulphate, the amount increasing with the depth of color. The color of the solution alone would be ample evidence that the nickel is present in other than its usual condition, while the presence of a powerful oxidizing agent is shown by the fact that the pink solution will liberate both iodine and bromine instantaneously from their salts with a simultaneous change of color from pink to green. Chlorine is also liberated from chlorides, though this takes place much more slowly. It is certain that we must have here either a simple or a complex nickelic sulphate.

Although this solution of nickelic sulphate reacts as such a powerful oxidizing agent, it undergoes spontaneous reduction much more slowly than does the acetate compound. If kept cold, this pink solution retains its color for days. Sulphurous acid, ferrous sulphate, and practically all other reducing agents, reduce it instantly in the cold. Upon heating to boiling, a spontaneous reduction takes place. Sodium hydroxide solution precipitates green nickelous hydroxide. This apparent exception to the reaction we should expect of a nickelic salt is readily accounted for when we remember the large amount of heat liberated by the reaction between a strong solution of a bisulphate and sodium hydroxide. This heat would, of course, cause the spontaneous reduction of the nickelic compound before it could

be precipitated as the hydroxide. Organic solvents added in the hope of precipitating the nickelic compound, caused its immediate reduction.

The color of the nickelic sulphate solution is interesting. It resembles in this respect almost exactly a somewhat dilute solution of a cobaltous salt. When it is remembered that trivalent cobalt in the form of cobaltioxalate yields nickel-green solutions, it will be seen that in compounds of both these metals we have an exact reversal of color according to the degree of oxidation.

The red or pink color of the solution of nickelic sulphate very readily explains the color changes found in the filtrate obtained during its formation. At first all is nickelous nickel, hence the green color; as nickelic sulphate is formed its pink shade neutralizes the green more and more, giving finally a solution looking like a mixture of nickel and cobalt. As more nickelic and less nickelous compound is formed, the color of course changes to pink. That there is always a certain amount of nickelous salt present is evidenced by the fact above mentioned that upon standing, an increase in the depth of pink color takes place, accompanied by the deposition of a green crystalline salt, which upon examination proves to be a neutral double sulphate of nickel and potassium. After a day or two this deposition of the nickelous double sulphate practically ceases and a brick-red, apparently amorphous powder is deposited, while the solution slowly loses its color.

This red powder is insoluble in water, but dissolves readily in sulphurous acid, yielding a green solution. It certainly contains trivalent nickel, being either the simple sulphate or possibly an alum. The amount so far obtained has been too small to analyze. Work is being continued upon this compound and it is hoped that an analysis of it can be reported before long.

Treatment of cobaltic hydroxide with potassium bisulphate solution will not yield a cobaltic sulphate. A reduction invariably occurs, seeming to indicate that cobaltic sulphate is less stable than the corresponding nickel salt.

THE ESTIMATION OF MINUTE QUANTITIES OF ARSENIC.

By H. B. Bishop.

Received December 12, 1905.

The determination of small amounts of arsenic has been the subject of considerable investigation during the past few years and the test that has received special attention and elaboration is the modified Marsh test. The result has been to perfect this method to such a point that for simplicity and sensitiveness it leaves little to be desired.

Perhaps the most thorough and satisfactory work on this subject that has recently appeared is that of G. Lockemann.[1] His observations upon the necessary precautions and the sensitiveness of the Marsh test have been verified by us and a mirror has been obtained with 1/10,000 mg. arsenic, which is as small an amount as has been detected by him and others.

It is to be noted that the Marsh test is only a part of an arsenic determination and that the preparation of a sample for such a test is often a much more difficult part of the operation. Most substances to be analyzed require a preliminary treatment to obtain the arsenic in a soluble form, free from interfering substances and in a suitable volume. When solution is obtained by a long and tedious oxidation, separation made by a precipitation method or concentration made by evaporation at a high temperature, numerous sources of error arise which necessitate the greatest vigilance to obtain reliable results. The smaller the quantity of arsenic, the greater the difficulty, for it is not only more easily lost but also more easily multiplied by the use of numerous arsenical reagents.

While trying to increase the delicacy of the determination of arsenic in sulphuric acid, a number of experiments were tried to test the accuracy of the evaporation method of concentration. In analyzing sulphuric acid of such purity that a few cubic centimeters do not show any arsenic, it has been customary to take a large sample and evaporate to a small volume suitable for the Marsh apparatus. It was thought that during such a long evaporation small amounts of arsenic might be lost and escape detection. Accordingly, known amounts of arsenic were added to 250 cc. samples of sulphuric acid which previous analysis by evapora-

[1] Z. angew. Chem., 1905, 416.

ting and applying the Marsh test had shown to be arsenic-free. When 0.000006 per cent. arsenic was added about a half was recovered, and in samples to which 0.000004 per cent. arsenic had been added the arsenic escaped detection, although the sensitiveness of the Marsh test at this time was 0.000001 per cent. arsenic or 0.004 mg. When it was found that these small amounts were volatilized so easily, the method which naturally suggested itself was to distil the arsenic under conditions which would be most favorable for its removal. The well-known method of distilling with ferrous chloride and hydrochloric acid was tried but the result was not satisfactory, as ferrous sulphate was precipitated and produced so much bumping that its use was abandoned. In the method finally adopted, a mixture of hydrochloric and sulphurous acids is forced through a capillary tube into the hot concentrated sulphuric acid. After distilling for one hour while absorbing the escaping gas in water, the distillate containing arsenious chloride, hydrochloric and sulphurous acids is oxidized with potassium chlorate, evaporated on the steam-bath and the Marsh test applied.

SEPARATION OF ARSENIC BY DISTILLATION.

The apparatus shown in Fig. 1 has been devised for carrying out the distillation.

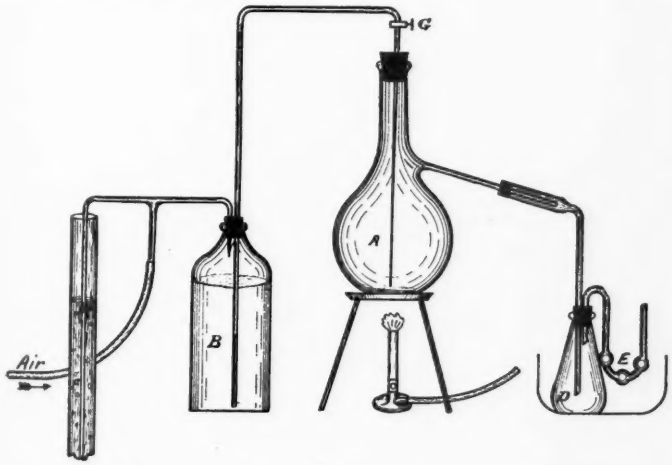


Fig. 1.

The sample is poured into the distilling flask *A* which is connected by a glass tube with the supply bottle *B* containing the sulphurous-hydrochloric acid mixture. The glass tube is provided with a glass stop-cock *C* for regulating the supply of acid and is drawn to a capillary extending to the bottom of *A*. If this tube is not drawn to a capillary, it is liable to break at the surface of the hot sulphuric acid. The side arm of the flask *A* is connected through an adapter with a receiver *D* which has a *U*-tube connection *E* to afford complete absorption of the gas. *D* and *E* are immersed in a basin of cold water. Some pressure is required to force hydrochloric acid through a capillary tube into hot sulphuric acid, and this is obtained by means of compressed air which is connected with *B* and *F* by a **T**-tube and exerts a pressure in *B* proportional to the height of the column of water in *F* (about 3 feet) through which it bubbles. The sample of sulphuric acid (about 95 per cent. H_2SO_4) is heated to 150–200° C. and the supply of the sulphurous-hydrochloric acid mixture regulated so that 50 to 75 cc. are used during a distillation of one hour. The small bubbles of gas formed at the end of the capillary permeate to all parts of the sample, keeping it stirred and in escaping carry the arsenious chloride into the receiver *D* where the gases are absorbed in about 50 cc. of cold water.

The first distillate usually contains all the arsenic, a second sometimes a trace, while a third and even a fourth distillation can be made to prove its complete removal and the absence of arsenic in the apparatus and reagents.

The distillate in *D* and *E* is poured into a casserole, oxidized with a pinch of potassium chlorate and evaporated on the steam-bath to 5–10 cc. and until all free chlorine has been expelled. It is then washed into the Marsh apparatus with a few cubic centimeters of 15 per cent. sulphuric acid.

In constructing the apparatus rubber connections have been avoided, and corks have been used in the bottle and flasks, as small amounts of arsenic have been traced to the use of rubber.

MARSH TEST.

The apparatus shown in Fig. 2 represents the most sensitive form used in this work.

The capacity of *A* is about 10 cc. and is provided with a ground glass stopper which can be removed for charging and cleaning.

The lower end of *A* communicates with a funnel tube *C* having a glass stop-cock. *D* is a side arm tube filled with neutral calcium

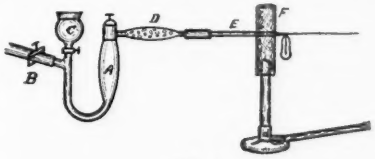


Fig. 2.

chloride for drying the gas, and to it is attached a hard glass tube *E*. This is drawn to a capillary and passes through a wire gauze chimney *F* at which point it is heated by a Bunsen burner.

To make a test, a few pieces of copper-plated zinc are placed in the tube *A* and the air is removed from the apparatus by a stream of carbon dioxide, obtained from a cylinder, entering at the tube *B* and regulated by a screw pinch-cock. After running for a few minutes it is stopped and the sample introduced through *C*. The arsine is decomposed by passing through the heated tube and the arsenic deposits in the capillary at a point cooled by a wet cotton string wound once around the tube and dipping into a small tube of water. Each test is allowed to run for one hour, observing the same conditions as in preparing the standard mirrors, and by comparing the mirror thus obtained with the standard set, the amount is estimated.

REAGENTS.

Ordinary chemically pure hydrochloric acid contains so much arsenic that it is entirely unfit for use in this work without previous purification. This is done by distillation, keeping it well oxidized by the addition of potassium chlorate. Since authorities differ in their ability to prepare arsenic-free hydrochloric acid in this way, it may be well to describe the apparatus used. It consists of a large supply bottle containing hydrochloric acid oxidized with potassium chlorate which is fed through a siphon into the bottom of a 2-liter distilling flask containing about 500 cc. of concentrated sulphuric acid. The flask is gently heated and the escaping hydrochloric acid carrying some chlorine is scrubbed and dried by bubbling consecutively through two more 2-liter flasks containing about a liter each of cold concentrated sulphuric acid and finally absorbed in a bottle of dis-

tilled water immersed in a cooler. By introducing a little chlorine in this way with the hydrochloric acid, the arsenic is kept oxidized, in which form it is not volatile at the temperature used, and any arsenic that might be mechanically carried over is removed by the sulphuric acid scrubbing. The resulting acid 20–22° Bé. is saturated with gas obtained from a cylinder of liquid sulphur dioxide, which removes the free chlorine. The reagent thus formed, if not absolutely arsenic-free, contains less than enough to affect an analysis as proved by blank determination. The same holds for the small amounts of potassium chlorate and sulphuric acid that are used in oxidizing the distillate and in making the Marsh test.

Arsenic-free shot zinc, such as is used in the Marsh test, is usually so pure that it does not react readily with acid, and the most satisfactory method of obtaining zinc that will give a good evolution of gas is to treat it as recommended by Lockemann with a 0.5 per cent. solution of copper sulphate which has been recrystallized. The zinc, black in appearance, is washed with water, dried on a filter-paper and preserved in a closed vessel until wanted for use. The only other reagent used is calcium chloride which as Lockemann also notes should be neutral. The ordinary dry chemically pure calcium chloride on the market is alkaline and when used in this form interferes with the sensitiveness of the test. It is therefore dissolved by heating with a small amount of water and neutralized or made slightly acid with hydrochloric acid, evaporated in a casserole while stirring until it begins to solidify, the stirring being continued while it cools so as to produce small lumps, the neutrality of which is proved by testing with phenolphthalein. It is then put into a closed vessel to preserve it till needed.

The arsenic solution used for preparing the standard mirrors is made by dissolving 1.320 grams of pure arsenious oxide (=1 gram arsenic) in 25 cc. of sulphuric acid and 10 cc. of nitric acid. When the arsenic has dissolved, water is added and the solution evaporated on the steam-bath to expel the nitric acid. It is then successively diluted and divided until a solution containing the desired amount of arsenic is obtained. For an apparatus of the size described, the largest mirror is made by using an amount of the solution corresponding to 0.01 mg. arsenic and for the smallest 0.0001 mg. arsenic.

EXPERIMENTAL.

ARSENIC IN SULPHURIC ACID.

In order to test the sensitiveness and accuracy of this method, 2-liters of 95 per cent. chemically pure sulphuric acid were freed from arsenic by distilling as described above until the final distillate did not show any arsenic, then 0.004 mg. of arsenic was added and by means of the above method, it was recovered and accurately determined. This is a determination of one part of arsenic in a billion of sulphuric acid or 0.0000001 per cent. arsenic. A sample of special sulphuric acid was subsequently analyzed and duplicate analyses showed it to contain 0.000,-00006 per cent. arsenic, which is probably the smallest percentage of any element that has been quantitatively separated and determined.

ARSENIC IN BRIMSTONE.

The determination of arsenic in brimstone has been even more difficult than in sulphuric acid, for it has been thought necessary to completely oxidize the sample before making the determination, and when the sample is a large one, a long treatment with large quantities of reagents is required. It was thought that this difficulty could be avoided by adding the sample of brimstone to purified sulphuric acid and then making the above separation and determination. When sulphur is added to hot concentrated sulphuric acid, it melts and floats through the acid in fine globules which having about the same density as the hot acid, are liable to settle, become superheated and crack the flask. Several flasks were broken in this way before the cause and remedy were found. It was apparent that the density of the acid was not high enough and it was therefore increased by the addition of sodium sulphate. Chemically pure sodium sulphate was tried but it contained so much arsenic that an equivalent amount of sodium hydroxide was substituted. To obtain the desired result 250 cc. of chemically pure sulphuric acid (95 per cent.) are poured into a casserole and 16 grams of chemically pure sodium hydroxide are cautiously added a little at a time. The heat of the reaction evaporates the excess of water so that when the solution has cooled, it is ready to be poured into the distilling flask and freed from arsenic as described above. The sample of brimstone is then added and after heating until a fine emulsion is obtained, the distillation is made and the arsenic estimated by the Marsh test.

A sample of brimstone that had been carefully analyzed by oxidation with bromine and nitric acid, evaporated to expel oxidizing agents and found to contain 0.002 per cent. arsenic, was tested by this method and found to contain 0.010 per cent. arsenic. Another sample of brimstone in which arsenic could not be detected when 25 grams were oxidized with fuming nitric acid, evaporated to expel nitric and tested in the Marsh apparatus, was analyzed by the above method and found to contain 0.00002 per cent. arsenic.

ARSENIC IN ORGANIC MATTER.

Most methods that have thus far been proposed for the determination of arsenic in organic matter have required its preliminary destruction by oxidation, fusion or combustion, and any one who has tried these methods is fully aware of the difficulties encountered.

While determining arsenic in sulphuric acid it seemed possible that organic substances might be added directly to the concentrated sulphuric acid, and have their arsenic removed by distillation without any preliminary treatment other than digestion in the acid to obtain solution of the arsenic.

To test this application of the method, a potato was obtained from a field where the vines had been sprayed with Paris green. The sample was thoroughly washed, dried, ground to a powder and 10 grams gradually added to 250 cc. of sulphuric acid in a distilling flask which a previous distillation and Marsh test had proven to be arsenic-free. After digesting hot for several hours and until the particles seemed thoroughly disintegrated, a distillation with the sulphurous-hydrochloric acid mixture was made, and a Marsh test of the distillate showed 0.01 mg. arsenic or 0.0001 per cent. arsenic. When we consider that on a wet basis this is only 0.00002 per cent., the potato containing about 76 per cent. of water, there is no need to fear arsenic poisoning from this source.

SUMMARY.

The separation of arsenic from concentrated sulphuric acid by distillation with sulphurous and hydrochloric acids and its subsequent estimation by the Marsh test, is a method well adapted for the determination of minute quantities of arsenic in sulphuric acid and, in general, in those substances that are soluble in or decomposed by hot concentrated sulphuric acid. The special

advantages are that large samples may be taken, comparatively few reagents are required and interfering substances are not introduced into the Marsh apparatus, so that it can be operated under standard and uniform conditions.

A MODIFIED WESTPHAL BALANCE FOR SOLIDS AND LIQUIDS.

By F. M. Williams.

Received December 8, 1905.

The advantages of the Westphal balance as a rapid and accurate means for the determination of the specific gravity of liquids are well recognized.

It occurred to the writer that this instrument might be so modified as to extend its use to the determination of the specific gravity of solids. Attempts have been made to use it with solids by means of heavy solutions, such as Thoulet's and Penfield's by diluting the liquid until the solid immersed will neither sink nor float, and then taking the gravity of the liquid in the ordinary way. But the maximum gravity obtainable by such solutions is about 4.5 and the operation is cumbersome and tedious.

The modifications in the old form may be readily seen from the accompanying drawing. It will be noted that the pointer has been lengthened and upon this at a distance equal to the length to the other arm, a notch has been placed for the reception of a special support carrying two pans, one below the surface of the liquid, and the other above. By this means an object may be weighed in air and then in liquid by interchanging the pans, or by transferring to the lower pan.

For convenience in adjustment a two-piece counterpoising weight is made to move along the threaded portion of the pointer. By having the counterpoising weight in two pieces one part serves as a lock-nut preventing accidental changes of adjustment.

A further modification tending to prevent wear upon the knife edges is a cam device for raising the beam and locking the same securely in place.

The balance has been made much more compact and portable by inserting a hinge joint in the upright standard arm, allowing the instrument to be folded to a space $2^3/_4 \times 2^3/_4 \times 10$ inches.

Owing to the comparatively unsatisfactory methods for the

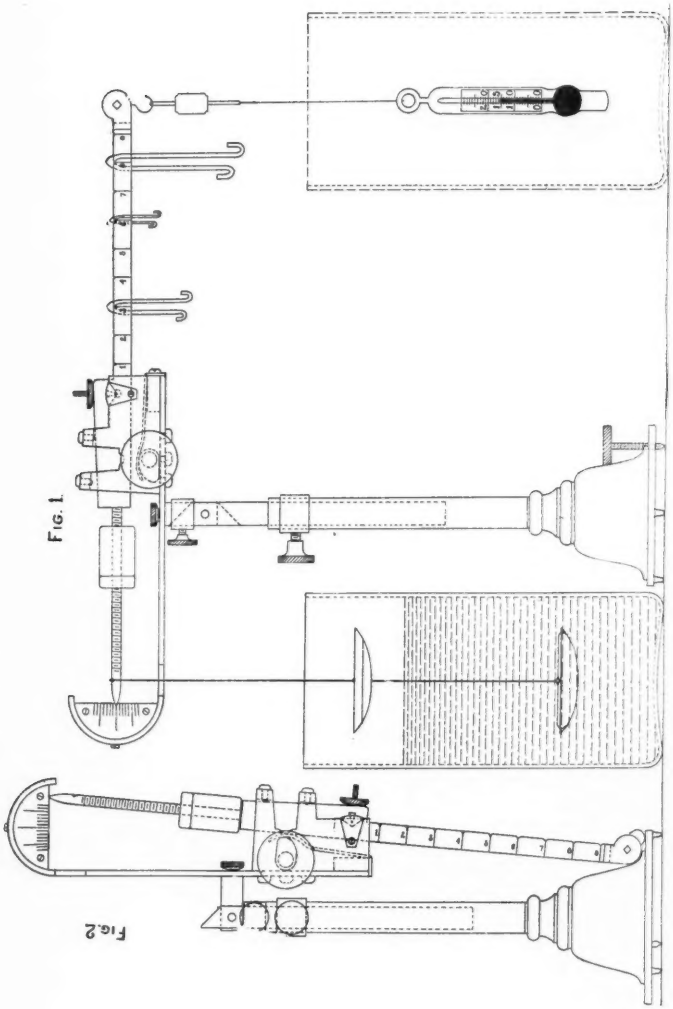


FIG. 1.

FIG. 2.

determination of the specific gravity of Portland cement, as for example, with the Le Chatelier apparatus, open to the objections of choking of the tube, inaccuracies of volumetric glassware, and the difficulty of maintaining a constant temperature during the operation, the modified form of the Westphal balance has commended itself most highly as an easy, rapid and accurate means for the determination of the specific gravity of cement and all other solids, whose composition is changed by immersion in water. With this instrument it is only necessary to weigh the substance in air, and then in some liquid such as kerosene, carbon tetrachloride, or carbon bisulphide, after which the specific gravity of the liquid used is determined in the ordinary way by means of the thermometer plummet.

For the specific gravity of minerals it has been found very rapid and accurate, permitting the substance to be in either the form of a fragment or powder.

It will be seen that the instrument combines in compact and portable form all the advantages of the original Westphal balance and the Jolly balance.

It may also be used as a portable analytical balance for loads up to 10 grams with a sensibility of 0.5 mg.

A PERCOLATOR FOR USE IN ASSAYING DRUGS.

By Frank R. Eldred.

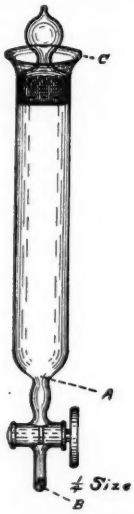
Received November 29, 1905.

The percolator here described has been in use in this laboratory for two years, during which time it has proved to be a very useful piece of apparatus.

Moistening or macerating a drug in one vessel and then transferring to another for extraction is a tedious operation always involving danger of loss. The dry drug can be placed in this percolator and the entire operation of maceration and extraction can be conducted without transfer.

In using this percolator (Fig. 1), a plug of cotton is packed tightly below the constriction *A*, by means of a wire which may be sharpened on one end and provided with several barbs for removing the cotton. The dry drug is placed in the percolator, the solvent is then added, the stopper inserted, and the whole thoroughly shaken. During the maceration the stopper is held

in place by a spring clip. If the stopper is removed carefully when the maceration is finished, the small amount of solvent which may be forced up around the stopper can be retained in the



funnel-shaped top, *C*, and washed down by a jet of the solvent, most conveniently produced by a Schuster's dropping-bottle, the heat of the hand being sufficient to expel a volatile solvent such as ether or chloroform. A plug of cotton is then inserted and pressed down with a glass rod, thus removing the particles of drug from the sides of the percolator and packing the drug for percolation. The rate of flow of the percolate can be regulated by the stop-cock, while the funnel top serves to hold the stopper in an inclined position, thus preventing undue evaporation of the solvent.

The percolators in use in this laboratory have a total length of about 30 cm., and a capacity of about 100 cc.

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INDIANAPOLIS, IND.

[Contributions from the Havemeyer Laboratories of Columbia University, No. 118.]

PROTEOLYSIS IN COWS' MILK PRESERVED BY MEANS OF FORMALDEHYDE.

By W. G. Tice and H. C. Sherman.

Received December 18, 1905.

Babcock and Russell, in 1897, announced the discovery of galactase, a trypsin-like enzyme secreted by the milk glands, and attributed to it rather than to bacteria or bacterial enzymes the principal part in the proteolysis which takes place during the ripening of cheese. Since that time the digestion of milk proteids by galactase and by bacterial enzymes has been studied in considerable detail as regards its relation to cheese-making, especially by Babcock, Russell, and associates,[1] Van Slyke and Hart,[2] Freudenreich,[3] Jensen,[4] and Rogers.[5] Since in most of the experiments upon milk, ether or chloroform has been used to suppress bacterial action, the following observations upon milk preserved by means of formaldehyde are believed to offer some points of interest in connection with the more detailed studies of proteolysis which are being carried out elsewhere.

Samples of milk which had been treated with formaldehyde (about 1 : 1000) within two hours after milking, and which had been opened, mixed, and analyzed within the next few days, were subsequently kept in tightly stoppered bottles at laboratory temperature, usually exposed to diffused but never to direct sunlight. Since the original reason for thus preserving the samples was simply to provide for possible repetitions of the chemical analysis, no special precautions were observed regarding the exact amount of formaldehyde added or the time elapsing in each case before the final sealing of the sample. It has, however, been shown[6] that formaldehyde disappears only slowly when added to milk in such large proportions as were here used, and there is little doubt that each of the samples contained 0.07 to 0.10 per cent. of formaldehyde when finally set away, so that

[1] Reports of the Wis. Agr. Expt. Station, 1897–9.

[2] Bulletins 203, 219, 231, 233, 236 of the N. Y. State Agr. Expt. Station.

[3] Landw. Jahrb. Schweiz, 14, 49 (1900).

[4] Ibid., 14, 197 (1900).

[5] Bull. 62, Bureau of Animal Industry, U. S. Dept. Agr.

[6] Williams and Sherman : This Journal, 27, 1497 (1905).

any organisms or enzymes originally present or gaining access to the milk during the analysis[1] must have resisted the action of that amount of formaldehyde in order to have brought about the changes which were subsequently observed. Almost without exception such samples have remained entirely normal in appearance for about a year,[2] after which the milk begins to lose its opacity immediately below the cream layer and continues very gradually to show more and more distinct evidence of digestion. Some samples which have stood three to five years contain relatively very small clots or precipitates of curd, which still appear to be diminishing in amount.

During the summer of 1904 several of these samples were examined for bacteria by Professor R. A. Wardall, of the South Dakota Agricultural College, who was at the time studying in this laboratory. Liquefying cocci, forming yellow colonies, were found in most of the samples examined. White colonies of cocci and bacilli were also occasionally found. In some cases no development was found either on agar or in lactose bouillon. In all cases in which bacteria were found, they were few in number and developed so slowly that a routine examination might easily have resulted in the samples being pronounced practically sterile.

Thus while there is strong probability that bacterial action was quite thoroughly suppressed, it cannot be assumed that the digestion taking place in these samples was a true autolysis due simply to the proteolytic enzymes secreted with the milk, since absolute sterility was not attained in most cases, and especially since it appears from the work of Freudenreich[3] that bacterial remains and spores may yield proteolytic enzymes in the absence of vegetative forms, and from the observation of Van Slyke and Hart[4] that the udders of some cows always contain liquefying bacteria which appear to secrete proteolytic enzymes in the milk even before it is drawn. We cannot, therefore, expect to distinguish sharply between the action of galactase and of bacteria

[1] In one case duplicate samples about a year old were analyzed, one having been used for chemical analysis as described, while the other had received the same amount of formaldehyde at the beginning and had never been opened. The results were practically the same.

[2] During this time the greater part of the formaldehyde originally present will usually have disappeared.

[3] Loc. cit.

[4] Bull. 203, N. Y. State Agr. Expt. Station.

or bacterial enzymes unless as the result of comparative studies of the nature of the fermentations taking place under different conditions.

Although none of our samples was large enough to permit identification of the end-products, it was thought that a general idea of the character of the proteolysis could be obtained through the determination of the distribution of the total nitrogen among the principal groups of products at different stages of the digestion. The methods adopted for the separation and estimation of the nitrogen compounds are practically those of Van Slyke and Hart[1], and are therefore only very briefly outlined.

Total nitrogen, as well as the nitrogen in each of the fractions, was determined by the Kjeldahl-Gunning method.

Casein was precipitated by diluting 10 grams of milk with 90 cc. of water and acidulating at a temperature of 40° with 1.5 cc. of 10 per cent. acetic acid; the precipitate was filtered, washed, and its nitrogen determined.

For the determination of albumin and syntonin the filtrate from the precipitation of casein was very carefully neutralized by caustic alkali, using phenolphthalein as indicator, and heated to boiling until the precipitate settled, when it was filtered, washed and the precipitate treated for the determination of nitrogen.

The filtrate from the precipitation of albumin and syntonin was heated to 70°, acidulated with 1 cc. of 50 per cent. sulphuric acid, then saturated with zinc sulphate, filtered, and the precipitated proteoses washed with a saturated zinc sulphate solution and finally determined by the Kjeldahl-Gunning method.

The filtrate from the proteoses was saturated with bromine and the precipitate washed with bromine water and determined as "peptones by bromine."

For the determination of peptones and of amino and ammonium compounds two portions of the original sample of milk were treated separately with tannin and with phosphotungstic acid as follows: (1) To 40–50 grams milk in a 250 cc. flask, add 1 gram sodium chloride and 150 cc. of water, and then precipitate the proteids by adding a 12 per cent. solution of tannin, shaking after each addition and carefully avoiding any considerable

[1] Bull. 215, N. Y. State Agr. Expt. Station; Amer. Ch. J. 29, 150 (1903).

excess of the reagent. Finally dilute to volume, filter, and determine nitrogen in 50 cc. of the clear filtrate. The nitrogen of the precipitate minus that of the casein, albumin, syntonin, and proteoses already determined is considered as belonging to "peptones by tannin." The nitrogen in the filtrate is taken as a measure of the "amino-compounds and ammonia by tannin."

(2) To 40–50 grams of milk in a 250 cc. flask add 150 cc. of water, 5 cc. concentrated sulphuric acid, and a 30 per cent. solution of phosphotungstic acid as long as a precipitate continues to be formed; then fill to the mark and complete the determination and the calculation of the results as in the case of the tannin precipitation.

On analyzing four samples of the same lot of milk eleven months old, two of which had stood at room temperature throughout, while two had been kept at 38° to 40° during the greater part of the last twelve days, no variation of results attributable to this difference of temperature could be found. It was therefore assumed that fluctuations of room temperature could have no appreciable effect upon the course of the proteolysis.[1] The average of these four analyses is taken as a basis for comparison in considering the nature of the changes which occur as digestion advances.

The accompanying table shows the principal results obtained.

The distribution of nitrogen found in the different samples indicates that the albumen was largely digested before the original amount of casein was appreciably reduced, but that subsequently, as digestion advanced and the casein diminished, the proportion of nitrogen existing as albumin and syntonin changed but little, the increase appearing first in the proteoses, then in the peptones and amino-compounds. In the last sample the proteoses and peptones had evidently been very largely broken down into amino-compounds, although small amounts of casein and acid albumin still remained. In general only a little more nitrogen was precipitated by phosphotungstic acid than by tannin, indicating that the precipitation of peptones by tannin must have been

[1] Jensen (loc. cit.) also found that milk containing formaldehyde digested about as rapidly at room temperature as at 35°, apparently because the stimulation of the galactase by the higher temperature is counterbalanced by the fact that formaldehyde affects that enzyme more injuriously in warm than in cold solution.

DISTRIBUTION OF NITROGEN IN SAMPLES OF MILK PRESERVED BY MEANS OF FORMALDEHYDE.

	Quadruplicate sample. 11 months old.	Sample No. 5.[1] 17 months old.	Sample No. 6. 26 months old.	Sample No. 7. 43 months old.	Sample No. 8. 28 months old.	Sample No. 9.[2] 37 months old.	
Lactose, per cent	4.25	4.37	4.46	4.46	4.68	4.76	
Estimated loss of lactose, per cent	0.31	...	0.39	0.38	0.18	0.15	
Acidity calculated as lactic, per cent.	0.24	0.21	0.31	0.54	0.84	1.43	
Percentage of the total nitrogen, found as						A.	B.[2]
Casein	80.6	73.7	73.7	11.4	3.7	4.5	17.9
Albumin and syntonin	5.0	4.4	6.3	6.8	5.5	4.8	4.2
Proteoses	6.1	14.2	11.1	24.9	29.9	12.3	10.6
Peptones by bromine	0.6	0.9	2.3	10.1	10.7	...	...
Peptones by tannin	1.9	1.7	3.0	9.1	...	1.6	1.4
Peptones by phosphotungstic acid	2.2	1.9	5.2	10.7	...	...	...
Amino acids, etc., by tannin	6.4	5.9	5.9	47.8	50.2 (by dif.)	76.8	65.9
Amino acids, etc., by phosphotungstic acid	6.1	5.7	3.7	46.2		...	...

nearly, if not quite, complete and that only small amounts of diamino-acids, precipitable by phosphotungstic acid but not by tannin, could have been present in these samples.

Babcock, Russell, Vivian and Hastings[3] found a similar small difference between the tannin and phosphotungstic acid precipitates in milk digested by galactase, while in samples digested by bacterial enzymes the differences were much larger. Moreover, in our experiments relatively large amounts of proteoses were found at a rather advanced stage in the digestion, a result similar to that obtained by Babcock and associates in galactase proteolysis, but entirely different from that of bacterial digestion of milk. The proteolysis which had taken place in our samples,

[1] A commercial sample treated with formaldehyde when about one day old and not subsequently opened. All of the other samples had been treated as previously described.

[2] This sample contained a small lump of very tough curd resembling a corroded rubber stopper. Column A gives the results of analysis of the sample without this lump; in column B the figures are recalculated on the assumption that all of the nitrogen in the lump was in the form of casein. For most of the determinations upon this sample we are indebted to Mr. W. N. Berg.

[3] Ann. Report Wis. Agr. Expt. Station, 1899, p. 165.

therefore, agrees in essential features with that brought about by Babcock and Russell's galactase, although in view of the work of Van Slyke and Hart, Freudenreich, and Jensen, it appears probable that in both cases bacterial enzymes may also have taken part in the digestion.

Sample No. 8 preserved by the addition of 0.1 per cent. formaldehyde developed an acidity corresponding to 0.84 per cent. lactic acid in twenty-eight months, and during this time lost only 0.18 per cent. of milk-sugar, or less than 4 per cent. of the original amount, while 95 per cent. of the original casein had undergone digestion. In experiments made by A. W. Hahn and A. J. Mettler in this laboratory upon samples of milk preserved by the addition of 0.1 per cent. sodium fluoride, sodium salicylate, or hydrogen peroxide, the total acidity calculated as lactic acid has never equaled the amount of lactose destroyed, while up to the point at which 25 to 30 per cent. of the original lactose has disappeared, no marked digestion of casein has ever been noticed.

These analyses, therefore, in addition to showing the general nature of the very extensive proteolysis which had taken place, afford a striking illustration of the effect of an added antiseptic in determining the character of the fermentation which subsequently occurs in the milk.

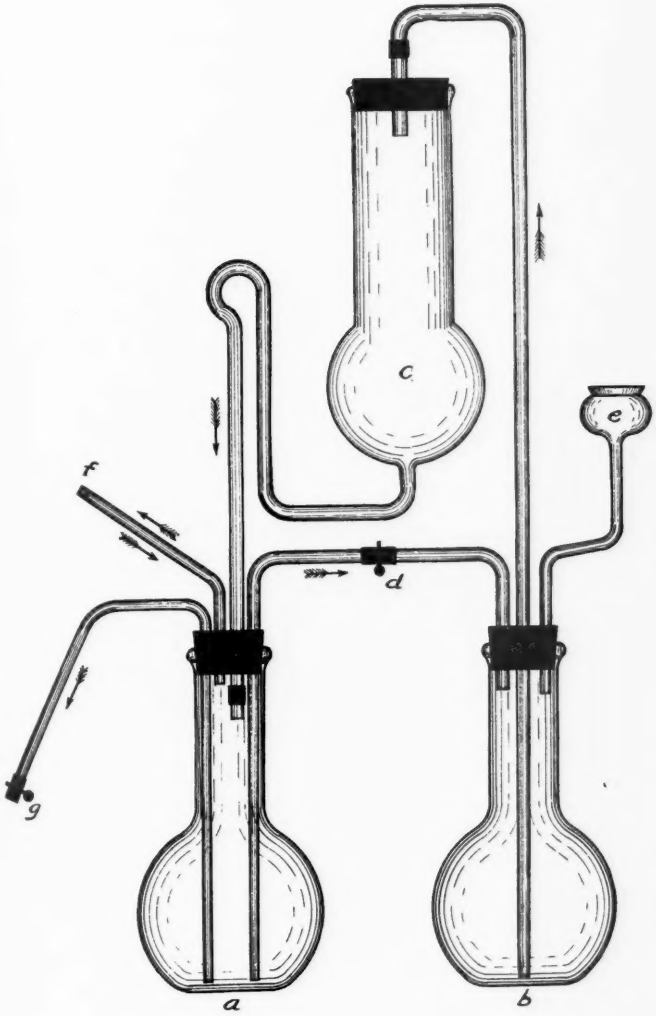
EXTRACTION APPARATUS.

By Allen Rogers.

Received December 11, 1905.

The author has obtained very excellent results by use of the herein-described apparatus in the analysis of such substances as tea, coffee, tannin and so on, where an aqueous infusion is necessary.

Two flasks *a* and *b* are employed and may be of any size desired. From the bottom of *b* a glass tube connects with *c* which contains the material to be extracted; at the end of *c* is a Bunsen valve. To charge the apparatus the clamp *d* is opened and water introduced through *e*; the clamp *d* is then closed, and suction applied at *f*, thus causing the liquid to pass over the material in *c*. The solution having passed from *b* to *a* the clamp *d* is again opened, and by blowing at *f* it is forced back into *b*. When a concentrated solution has been obtained in *a* it may be removed


c
e
f
d
g
a
b

by opening *g* and blowing in at *f*. A fresh supply of water is then added, and the process continued until the extraction is completed.

The flasks are heated on a water-bath, thus having the advantage of reproducing the conditions as they exist in commercial processes.

The suction is secured by means of a filter-pump, and can be regulated so that the solvent passes over the material drop-wise. The time required for the liquid to pass from *b* to *a* in this manner is about fifteen minutes, thus necessitating a minimum amount of attention. The period of extraction is much less than by means of the Soxhlet or other methods in common use, and obviates the danger of decomposition in the tannic acid. It will be seen also that the apparatus is applicable to any form of extraction, and the temperature may be regulated to suit the various conditions.

A REAGENT IN THE CHEMISTRY OF FATS.[1]

By E. Twitchell.

Received December 20, 1905.

(FIRST PAPER.)

In a previous paper[2] I described a new series of sulphonic acids of the stearic radical combined with various aromatic radicals. These compounds are stable at 100° C. and act as catalytic agents in causing the hydrolysis of fats. At 100° C. less than 1 per cent. of naphthalenestearosulphonic acid added to a mixture of a fat with an excess of water will cause an almost complete separation of the glycerol in eight to ten hours. Of course a continual mixing of the fat and water, as by boiling, is necessary.

Other sulphonic acids containing a higher fatty radical (acid or hydrocarbon) have the power of decomposing fat and water into fatty acid and glycerol at moderate temperatures, but the fatty-aromatic sulphonic acids above referred to are prepared more easily and with better yields. They are therefore used exclusively in my process of separating glycerol from fats on a large scale.

Stearosulphuric acid, prepared by treating oleic acid with a moderate excess of sulphonic acid, has most of the properties

[1] Read before the Cincinnati Section of the American Chemical Society, December 13, 1905.

[2] This Journal, **22**, 22.

of the above sulphonic acids, but it gradually decomposes at ordinary temperatures and quickly on heating to 100° C., and so cannot be used for the hydrolysis of fats.

The special catalytic action of these sulphonic acids, or "sulpho-fatty acids" can be explained as follows: They are soluble in water and their aqueous solutions dissolve fatty bodies, acting like soap solutions. At the same time they are acids which are electrolytically dissociated to a high degree. Therefore, on mixing a glyceride with water and adding a little sulpho-fatty acid, some of the fat will go into solution in the water, and this water will contain hydrogen ions due to the electrolytic decomposition of the sulpho-fatty acid. An ester dissolved in water is rapidly dissociated in the presence of hydrogen ions which can be supplied by adding to the solution a small quantity of a strong mineral acid. A glyceride of a higher fatty acid, being insoluble in water, can not be acted on in this way, but when it is made soluble by the sulpho-fatty acid it behaves just as any soluble ester. The following observations prove this. A soluble glyceride such as triacetin, is rapidly hydrolyzed when boiled with water containing a few drops of a strong mineral acid, while an insoluble glyceride, such as triolein, is not appreciably hydrolyzed at 100°, even when large quantities of strong mineral acids are added to the water (Lewkowitsch has shown that if a very strong solution of hydrochloric acid, sp. gr. 1.16, is employed hydrolysis will take place at a moderate speed, but with this extreme concentration there is probably some other cause for the hydrolysis than the mere presence of hydrogen ions), but on adding a sulpho-fatty acid, thus making the triolein soluble in water, the hydrogen ions become as active as they are with triacetin.

A comparison of the hydrolyzing power of naphthalenestearosulphonic acid and of hydrochloric acid on a soluble glyceride, triacetin, is given in the following table. A half normal aqueous solution of triacetin (8.63 per cent.) was boiled in a flask with a reversed condenser, in one case alone, then with enough hydrochloric acid added to make the solution $^1/_{75}$ normal hydrochloric acid, then with $^1/_{75}$ normal naphthalenestearosulphonic acid. Small measured quantities of the solution were drawn from the flask at intervals and the acetic acid liberated was titrated. The results are expressed in percentages of a complete decomposition.

Time.	Decomposition in H_2O alone. Per cent.	Decomposition in $n/75$ HCl. Per cent.	Decomposition in $n/75$ $C_{10}H_6SO_3HC_{18}H_{35}O_2$. Per cent.
Half hour.....	.....	31.85	35.02
One hour.....	0.80	54.12	59.93
One and a half hours.....	.....	69.64	.....
Two hours.....	2.24	80.69	83.21
Two and a half hours.....	.....	.....	.....
Three hours	.....	92.41	92.06
Three and a half hours...	2.53	.....	.....
Four hours.....	.....	98.02	94.59

These experiments were not made with the greatest care but they show plainly enough that both acids are about equally effective, that is, both are about equally dissociated electrolytically and on a soluble ester have the same hydrolyzing power. If in place of triacetin we substitute a glyceride insoluble in water, such as an ordinary fat, then hydrochloric acid of the above concentration has practically no hydrolytic effect, while naphthalenestearosulphonic acid acts with about the same power as it does on the soluble esters.

The peculiar properties of sulpho-fatty acids can be applied in other ways in the chemical treatment of fats. Their property of dissolving in both fatty acid and water and rendering these two mutually soluble can be used to cause the separation of solid and liquid fatty acids.

When a melted mass of mixed fatty acids is allowed to cool the solid constituent crystallizes out, forming a porous mass holding the liquid fatty acid in its pores. If to the melted fatty acid a small quantity of a sulpho-fatty acid has been added, this will remain dissolved in the liquid after the solid has crystallized out pure. The liquid fatty acid will thus become slightly soluble and by simply treating with water can be washed out of the mixture, partly in solution but mainly as an emulsion. In both forms it passes through an ordinary filter-paper while the solid fatty acid is retained.

I have used this process in the laboratory in the following way for the separation of stearic and palmitic from oleic and linolic acids in tallow and other fats.

To 5 grams of the crystallized fatty acid is added about $^1/_{10}$ gram of naphthalenestearosulphonic acid, which is conveniently kept and used in the form of a 10 per cent. aqueous solution. A little dilute sulphuric acid (containing about $1^1/_4$ per cent.

H_2SO_4) is added and the mass is thoroughly ground up with a pestle. Twenty to 30 cc. in all of the dilute sulphuric acid are then added and the mixture allowed to settle. In a little while a copious layer of oil will rise to the surface. The mixture is then filtered through an ordinary filter-paper with the help of a filter-pump, pouring off the oil first and allowing it to be drawn through before the rest is brought on the filter. The mass on the filter-paper is then washed with the same dilute sulphuric acid solution until the filtrate is no longer cloudy. Eighty to 90 per cent. of the liquid fatty acid contained in the mixture will have been removed by this treatment. To extract the remainder the impure solid fatty acids must be removed from the filter and treated again with naphthalenestearosulphonic acid and dilute sulphuric acid as before. It requires several such treatments to extract the last few percentages of liquid fatty acid.

The crystalline mass on the filter-paper is finally washed with pure water, then collected and dried in any convenient manner, weighed and otherwise examined.

The object of the sulphuric acid in this process is to reduce the solubility of the sulpho-fatty acid in water and cause it to nearly all dissolve in the oil and not in the water as it would if pure water were used. If the proper amount of sulphuric acid is used, the acid water has still a strong tendency to emulsify with the oil containing the sulpho-fatty acid and will wash it out of the solid fatty acid mechanically, while pure water would dissolve out the sulpho-fatty acid before all the oil was washed out. The success of this method of separation depends largely on this equilibrium between the fatty and aqueous solutions of the sulpho-fatty acid. Instead of sulphuric acid any strong mineral acid may be used or, if instead of the sulpho fatty acid one of its soluble salts, which has the same property of dissolving in both fatty acid and water, has been made use of, then the same salt of a strong acid should be added to the water.

At ordinary temperatures the liquid fatty acids extracted from the mixture are not quite free from solid fatty acids. The amount thus lost corresponds to the solubility of the solid in the liquid fatty acids at the temperature of the operation. This error can be reduced to a minimum by conducting the operation at a temperature a little above the melting-point of oleic acid.

Stearosulphuric acid can be used for this separation, as at the

temperature of the work it decomposes only very slowly. However, I have found the mono-sodium or potassium salt of this acid just as efficient and much more stable.

Within the last few months a French patent has been issued to F. Lanza for the separation of solid and liquid fatty acids. Stearosulphuric acid, called in the specifications sulpho-oleic acid, is the reagent used in his process, which is very similar to the one described in this paper.

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE, DIVISION OF FOODS. SENT BY H. W. WILEY.]

STUDY OF APPLE MARC.[1]

BY W. D. BIGELOW AND H. C. GORE.

Received December 19, 1905.

GENERAL DISCUSSION.

APPLE marc, or the insoluble matter of the flesh of the apple, is composed mainly of parenchymous tissue, containing besides this only the somewhat lignified vascular bundles in small quantity, and a little albuminoid matter. For this reason apple marc affords a convenient material for study of parenchymous tissue, such tissue being, of course, much easier of study in the nearly pure form in which it occurs in the apple, than in the grains and grasses in which it occurs together with more complex tissue. Parenchymatous tissue has been very little worked with *per se*, notwithstanding the fact that it is the first tissue formed in plant growth, and therefore of extreme importance physiologically.

In our work with apple marc[2] we found that about 40 per cent. of the product was rendered soluble by boiling with water. This method of treatment, which has been used by Weisburg[3] and Wohl and Van Niessen[4] in their work with beet marc, is well adapted to the study of such products, because after the treatment not only the undissolved tissues, but the dissolved portions, can be readily recovered nearly unchanged and further examined. Acid or alkali treatment of course alters the composition of the dissolved material to a very much greater extent than water.

[1] Read before the Agricultural Section of the American Chemica So ciety, June 23, 1905.

[2] U. S. Dept. Agr., Bur. Chem., Bull. 94, p. 87.

[3] Neue Z. Rübenz, 21, 325 (1888).

[4] Z. Ver. Zucker-Ind. 39, 924 (1889).

The present work was undertaken in order to determine whether the portion of the marc made soluble by boiling with water, consists of one carbohydrate complex or of several. Two methods were proposed in our early work,[1] *viz.*, fractional extraction with boiling water whereby the portion first removed can be compared with those removed later; and fractional precipitation of the soluble product with alcohol. The first-named method has been employed in the work here recorded. The criteria used have been the yields of pentosans, of galactans, and the yield of reducing sugars calculated to starch when treated with hydrochloric acid as in the method for starch. The results show that one complex, a galacto-araban, is being gradually made soluble by the action of boiling water. This is shown in Table I. Since the sum of the yield of pentosans and the yield of galactans is considerably greater than that of reducing sugars calculated to starch, it is evident that the three-hour treatment with hydrochloric acid, as prescribed by the method for starch, does not give the maximum of reducing sugars.

TABLE I.—ANALYSES OF HOT WATER EXTRACTS OF APPLE MARC.

	Time of boiling.	Original dry marc. Per cent.	Protein ($N \times 6.25$). Per cent.	Pentosans. Per cent.	Galactans. Per cent.	Hydrolyzable carbohydrates calculated as starch. Per cent.	Ratio of galactans to pentosans.
First extract.....	½ hr.	17.32	3.16	38.8	31.6	53.4	0.81
Second extract.....	1 "	13.23	3.86	42.1	35.4	55.0	0.84
Third extract.....	1 "	5.53	5.26	36.1	29.9	48.8	0.83
Fourth extract.....	1 "	3.75	6.38	32.3	30.4	44.6	0.94

The must of apples, when treated with several volumes of alcohol, invariably gives a gummy precipitate. Preliminary experiments indicated that it would be worth while to collect a considerable quantity of such precipitate and determined therein the relation between the pentosan, galactan, and hydrolyzable carbohydrate contents for comparison with those found for the soluble portions of apple marc. The results are shown in Table II. It will be noted that the ratio of galactans to pentosans is much higher in this product than in the hot water extract of apple

[1] Loc. cit.

marc. If the alcohol precipitate of the must be supposed to be formed from some change in the cell wall whereby the less resistant portions of the tissue are partially resolved, it would seem that during the change a greater portion of the galactans is converted into compounds precipitable with alcohol than of the pentosans.

TABLE II.—ANALYSIS OF ALCOHOL PRECIPITATE OF APPLE MUST.

Protein (N × 6.25). Per cent.	Pentosans. Per cent.	Galactans. Per cent.	Hydrolyzable carbohydrates calculated as starch. Per cent.	Ratio of galactans to pentosans.
23.50	13.10	23.5	23.4	1.79

At this time in our work the high pentosan content relative to the total solids of "second pressing" ciders[1] was called to our attention by Messrs. Tolman and LeClerc. These were found to yield considerable quantities of precipitate when treated with alcohol. This precipitate contained from 39 to 65 per cent. of the pentosan content in case of the three samples of "second pressing" cider which we examined. One of these samples was converted into vinegar by one of the rapid process methods and examined at intervals during acetification. The alcohol precipitate remained practically unchanged in quantity and character during the acetification of the cider. These results are shown in Table III. It will be noted from Table IV that the ratio of galactans to pentosans is also higher in this product than in our preparations of hot water extracts of apple marc. In fermentation in heaps it is probably the wild yeasts which occur on the apples which attack the cell walls, breaking them down in such manner that a further yield of juice is obtained on a second pressing. The results are interesting in showing that possibly the action of yeasts on the cell walls of the apple marc in the pomace is similar to that of the life forces on the wall, an alcohol precipitate in which the galactan to pentosan ratio is high, being found in both cases.

[1] Prepared from apple pomace which had been allowed to ferment in large heaps for considerable periods of time. The pomace is again pressed, and a cider is obtained which is sometimes used for vinegar stock.

TABLE III.—PENTOSANS IN "SECOND PRESSING" CIDERS.

Serial number.	Date of analysis.	Pentosans. Grams per 100 cc.	Alcohol precipitate. Grams per 100 cc.	Pentosans in alcohol precipitate. Per cent. of precipitate.	Pentosans in alcohol precipitate Per cent. of cider.	Precipitable pentosans Per cent. of pentosans.
11533	April 22, '05	0.80	1.50	31.1	0.466	58.1
11533	May 1, '05	0.66	1.43	29.9	0.426	64.9
11533	" 17, '05	0.79	1.49	33.2	0.495	62.7

TABLE IV.—ANALYSIS OF ALCOHOL PRECIPITATE OF "SECOND PRESSING" CIDER.

Date of analysis.	Pentosans. Per cent.	Galactans. Per cent.	Hydrolyzable carbohydrates calculated as starch. Per cent.	Ratio of galactans to pentosans.
May 17, '05	33.2	46.5	55.0	1.40

Aside from the study of the hot water extracts of apple marc, and the relations of other products of the apple to them, *viz.*, the alcohol precipitate of the must, and the alcohol precipitate of "second pressing" ciders, the effect of the treatment with boiling water on the residual cellular material is of interest in showing to what extent the hot water treatment will affect the amount and character of the residues which are obtained by applying the method for crude fiber and the method for cellulose[1] after the treatment with hot water.

The percentages of crude fiber and of cellulose were determined in the marcs and in the insoluble residues left after extraction with hot water, the results being calculated in terms of the original marc. These results are given in Table V. It will be seen that the results obtained with the untreated marc are higher than those obtained with the residue from the hot water extraction. The products separated as crude fiber and cellulose from the original marc were found to be considerably richer in pentosans than those separated from the residue from the hot water extraction, a purer fiber and a purer cellulose being obtained. It is therefore evident that the methods employed for the determination of crude fiber and of cellulose do not separate cleanly the resistant from the non-resistant constituents of parenchymous tissue.

[1] "Cellulose," 2nd Ed., 1905, p. 95.

TABLE V.—CRUDE FIBER AND CELLULOSE IN APPLE MARC BEFORE AND AFTER HOT WATER TREATMENT. BASIS OF ORIGINAL DRY MARC.

	Crude fiber.	Pentosans in crude fiber.	Cellulose.	Pentosans in cellulose.
Untreated marc.....	30.90	2.92	40.19	5.51
Treated marc[1].....	27.34	2.21	34.82	4.20

METHODS EMPLOYED.

The methods of the Association of Official Agricultural Chemists were used for the analytical work—save that for the pentosan determinations the latest modifications of the method and the factors of Kröber[2] were used.

We were unsuccessful in applying the method for galactan to apple marc. No separation of mucic acid crystals was obtained, although the analysis of the hot water extracts of apple marc showed nearly 13 per cent. of galactan calculated on the marc. See Table VI. We did not, however, try the procedure of Wohl and Van Niessen.[3]

The material required for the work has been (*a*) hot water extracts from apple marc; (*b*) alcohol precipitate of fresh apple must; and (*c*) alcohol precipitate of "second pressing" ciders.

The methods of preparation of the above products were as follows:

(*a*) *Preparation of Hot Water Extracts from Apple Marc.*—A large sample of Rhode Island Greening apples was employed. These apples by March 30, 1905, the date at which the work was begun, were about at the end of their life history. They were free from starch, and many of the larger individuals were mealy. Some were browned about the core, indicating that physiological death was setting in. Such fruits were rejected. The remaining apples were cored and pared, all decayed and bruised places removed, and the sample ground in a meat grinder. The ground pulp was received in cloth bags from which the juice was pressed out. The marc remaining in the bag was thoroughly washed until free from sugar in the cloth bags by repeatedly adding water and pressing. It was then scraped from the bags, spread out on a large glass plate and dried over night at room temperature in a current of air from an electric fan. It was then ground

[1] 39.83 per cent. of original marc removed by hot water treatment.

[2] U. S. Dept. of Agr., Bur. of Chem., Bull. 73, 173.

[3] Z. Ver. d. Zucker-Ind. 39, 932 (1889); abst. in U. S. Dept. Agr., Bur. of Chem., Bull. 94, p. 74.

and passed through a 1 mm. sieve. The analysis of the product is given in Table VI.

TABLE VI.—ANALYSIS OF APPLE MARC. WATER-FREE BASIS.

	Per cent.
Pentosans	24.51
Extracted pentosans[1]	15.50
Extracted galactans[1]	12.96
Cellulose[2]	40.19
Crude fiber[3]	30.90
Reducing sugar	1.67
Protein	3.43
Ether extract	0.74
Ash	0.95

After preliminary trials which indicated the quantities of marc and water which could be successfully used, 100 grams of marc prepared as above were added to fifty times their weight of boiling water and the whole boiled for one-half hour under return condensers. Three flasks were used, two holding one and one-half liters each, and the third, two liters. Thirty grams of marc were accordingly added to each of the first two flasks, and 40 grams to the last.

At the end of the half hour's boiling, the flasks and their contents were rapidly cooled, the contents poured into clean cloth bags, and the bags squeezed to remove as much of the liquid as possible. The residues in the bags were washed by repeatedly soaking with water and pressing out. The filtrates and washings were combined and evaporated on the steam-bath, dried at 100°, weighed, ground, passed through bolting-cloth of about 0.5 mm. mesh, and again dried at 100°. The residues in the bags were then roughly weighed, the flasks charged with the original quantity of water less that held in the marc, the water heated to boiling, and the residue added. The time of the second, third and fourth boiling was one hour each. The extracts were treated as in the case of the product from the first boiling. The analyses of the hot water extracts are given in Table I.

(*b*) *Preparation of Alcohol Precipitate from Fresh Apple Must.*—The fresh juice from the above sample of apple pulp was whirled in a centrifugal machine which removed the small quantity of

[1] Sum of constituent in hot water extracts.

[2] Contains 5.51 per cent. of pentosans.

[3] Contains 2.92 per cent. of pentosans.

suspended materials, chiefly albuminous in character, which began to separate from the juice on standing in the air. On whirling, these were thrown down as a brown slimy sediment. To the supernatant liquors which were still turbid, but in which no more sediment would collect on whirling, was added with stirring an equal volume of 95 per cent. alcohol and the whole well shaken. A flocculent precipitate resulted equal to 0.3 per cent. of the original juice. The precipitate was settled in the centrifugal machine, and washed by repeated stirring with successive portions of alcohol and settling until no more yellow color and only traces of sugar were removed. The precipitate was then washed on to a filter with alcohol, allowed to drain (keeping the funnel covered with a watch-glass to prevent drying at the edges and consequent sticking to the filter-paper), separated from the filter-paper (it separates easily if kept moist with alcohol), and dried and weighed in a tared dish. It was then ground, passed through bolting-cloth, and dried at 100° C. The analysis of this product is given in Table II.

(*c*) *Preparation of Alcohol Precipitate from Second Pressing Ciders.*—The "second pressing" cider employed was obtained through Mr. Tolman of this laboratory. It had been made from apple pomace which had been fermented in heaps for fourteen days. To the clear cider four volumes of 95 per cent. alcohol were added, and the mixture well shaken. A finely divided white precipitate formed equal to 1.5 per cent. of the cider. This was separated from the mother-liquors by means of the centrifugal machine and washed by repeated stirring with alcohol and sedimentation. It was finally thrown on a filter, allowed to drain, transferred to a tared dish, dried and weighed. It was then passed through bolting-cloth, and dried at 100°.

CHARACTERISTICS OF PRODUCTS.

The hot water extracts from apple marc dry down as nearly transparent leaflets. The first extract was of a tough character but this property disappeared with successive extractions, the last extract being easily pulverized. They possess a slight acid taste, and dissolve in water to form viscid cloudy liquids. Alcohol precipitates the product from its solution in water as a jelly.

The alcohol precipitate from apple must appears as an opaque yellow-brown jelly-like mass. It dries down to a hard, easily pulverized dark brown product.

The alcohol precipitate of "second pressing" cider dries down to hard readily pulverized white masses. It is easily soluble in water, forming opalescent solutions very difficult to clarify. It possesses a marked acid taste.

SUMMARY.

The following points are determined.

(1) The hot water extract amounting to 40 per cent. of apple marc consists of one carbohydrate complex, a galacto-araban.

(2) The carbohydrate complexes in case of the alcohol precipitate of apple must, and in case of the alcohol precipitate of second pressing ciders, are both higher in galactan, relative to the pentosan content, than the hot water extracts of apple marc.

(3) The treatment with boiling water lessens the yield of crude fiber and cellulose, and at the same time gives a purer fiber and a purer cellulose.

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 117.]

ON 5-AMINO-4-KETODIHYDROQUINAZOLINE AND 5-AMINO-2-METHYL-4-KETODIHYDROQUINAZOLINE.[1]

BY MARSTON TAYLOR BOGERT AND VICTOR JOHN CHAMBERS.

Received December 14, 1905.

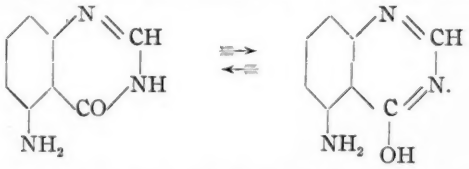
THE authors have prepared 5-amino-4-ketodihydroquinazoline and 5-amino-2-methyl-4-ketodihydroquinazoline by reducing the corresponding nitro compounds with stannous chloride and hydrochloric acid. The 5-amino-4-ketodihydroquinazoline is much more easily obtained than its 2-methyl derivative, since it is soluble in hot water and can thus be readily separated from the tin, hence most of the reactions carried out were with this quinazoline. Its hydrochloride, chlorplatinate, bibrom, acetyl, benzoyl and phenyluramino derivatives, were prepared and studied, as well as its reactions with nitrous acid, chloroform and potassium hydroxide, and with benzaldehyde. The phenyluramino derivative breaks up at high temperatures into carbanilide and what appears to be the diquinazolylurea. The 5-amino-2-methyl-4-ketodihydroquinazoline was more troublesome to obtain, and only its hydrochloride and chlorplatinate were prepared.

[1] Read at the General Meeting of the American Chemical Society, June 22, 1905.

In these aminoquinazolines, the amino group shows the usual aniline reactions so far as examined, while the miazine cycle exhibits its own characteristic properties. The compounds are easily soluble in solutions of the caustic alkalies, and are reprecipitated from such solutions by carbon dioxide or by mineral acids. With strong mineral acids they form salts. These salts are rather more stable than those of the corresponding unsubstituted quinazolines, but are also dissociated by boiling with much water.

EXPERIMENTAL.

5-Amino-4-ketodihydroquinazoline (*5-Amino-4-oxyquinazoline*),



—5-Nitro-4-ketodihydroquinazoline, prepared as described in a previous paper,[1] was added gradually to a hot solution of stannous chloride in concentrated hydrochloric acid, an excess (50 per cent.) of stannous chloride being used. The reduction proceeded rapidly. When all the nitro compound had been added, the solution was gently heated on the sand-bath for half an hour, and then poured into about ten volumes of water. The solution was neutralized by adding pieces of marble from time to time. It was then heated to boiling, filtered hot through a hot water funnel, and the undissolved portion repeatedly extracted with boiling water, adding these extracts to the filtrate. From this solution, on cooling, the aminoquinazoline crystallized in long, fine needles. The dimorphism noted in the case of the nitroquinazoline was not observed with this aminoquinazoline. The crystals of aminoquinazoline which separate from aqueous solution carry one molecule of water, and melt at 235–236° (corr.). They were analyzed with the following results:

Found: Water, 10.13 and 10.07; N, 23.5 and 23.6. Calculated for $C_8H_7ON_3.H_2O$: H_2O, 10.06; N, 23.4.

The compound is moderately soluble in water, alcohol, acetone or ethyl acetate, when boiling, but sparingly soluble in these

[1] This Journal, 27, 654 (1905).

solvents when cold. It is almost insoluble in ether, chloroform, carbon tetrachloride or petroleum ether. In aqueous solutions of the caustic alkalies it dissolves freely, and is reprecipitated from such solutions by carbon dioxide. It also dissolves in concentrated hydrochloric acid with formation of the hydrochloride. Both the crystals, and their aqueous or hydrochloric acid solutions, gradually redden and darken in the light.

Hydrochloride.—The aminoquinazoline was dissolved in warm dry ethyl acetate and treated with a stream of dry hydrogen chloride. The hydrochloride precipitated as a white granular powder, which soon darkened in the light. In a small amount of warm water it dissolves without decomposition, and on cooling needles separate. It is dissociated, however, by warming with much water.

Chlorplatinate.—The hydrochloride was dissolved in a little warm dilute hydrochloric acid, and a solution of chlorplatinic acid added. On cooling, the chlorplatinate separated in coarse yellow needles, carrying two molecules of water.

Calculated for $(C_8H_7ON_3.HCl)_2PtCl_4.2H_2O$: Water, 4.9. Found: Water, 5.1. Calculated for $(C_8H_7ON_3.HCl)_2PtCl_4$: Pt, 26.6. Found: Pt, 26.4.

Bibrom-5-amino-4-ketodihydroquinazoline (*Bibrom-5-amino-4-oxyquinazoline*).—A few grams of the aminoquinazoline were dissolved in warm water and treated with bromine water until no further precipitation occurred. The flocculent precipitate was filtered out, washed, dissolved in dilute potassium hydroxide solution, and reprecipitated by carbon dioxide. A white amorphous powder resulted, which was soluble in glacial acetic acid or in nitrobenzene, but insoluble in all other solvents tried. It did not crystallize well from either glacial acetic acid or from nitrobenzene. In the light, it gradually darkened, while the brominated acetaminoquinazoline, referred to below, was unaffected.

Calculated for $C_8H_5ON_3Br_2$: Br, 50.1. Found: Br, 50.2.

The position of the bromine atoms in the molecule was not determined, but in view of the usual orienting effect of the amino group, it is likely that they are at positions 6 and 8.

5-Acetamino-4-ketodihydroquinazoline (*5-Acetamino-4-oxyquinazoline*).—The aminoquinazoline was heated for a short time with acetic anhydride and the product recrystallized from dilute

alcohol containing a little acetic acid. Fine colorless needles were thus obtained, which melted at 285–286° (corr.) with darkening. The substance is soluble in warm acetone or alcohol, more readily in presence of a little acetic acid, but is very difficultly soluble in ether, chloroform, carbon tetrachloride or benzene.

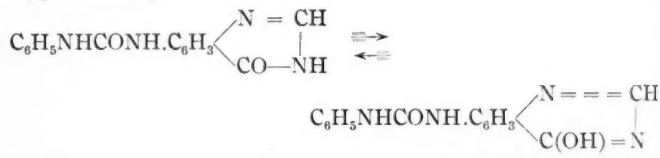
Calculated for $C_{10}H_9O_2N_3$: N, 20.7. Found: N, 20.9 and 20.9.

By the action of bromine water upon a dilute acetic acid solution of the acetaminoquinazoline a bromine derivative immediately resulted, but it has not as yet been further investigated or analyzed. It will be taken up later.

5-Benzoylamino-4-ketodihydroquinazoline (*5-Benzoylamino-4-oxyquinazoline*). — This substance, prepared from the aminoquinazoline and benzoyl chloride, was purified by solution in cold dilute alkali and reprecipitation with carbon dioxide. When recrystallized from alcohol, it appeared in glistening white needles or scales, which felted together when filtered. They melted at 263–264° (corr.), and showed approximately the same solubilities as the acetyl derivative.

Calculated for $C_{15}H_{12}O_2N_3$: N, 15.8. Found: N, 15.8.

5-Phenyluramino-4-ketodihydroquinazoline (*5-Phenyluramino-4-oxyquinazoline*).



—The aminoquinazoline was heated with excess of phenyl isocyanate for an hour in an oil-bath at about 170°. The crystalline quinazoline was thereby changed to a pale brown chalky mass. This was washed with dry ether, to remove excess of isocyanate, and purified by several recrystallizations from alcohol. Fine white needles were thus obtained: easily soluble in warm alcohol; slightly soluble in warm benzene; insoluble in chloroform, ether or petroleum ether.

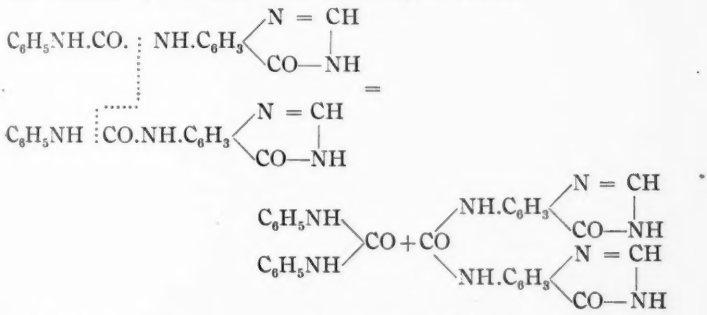
Calculated for $C_{15}H_{12}O_2N_4$: N, 20.0. Found: N, 19.7.

The behavior of this substance on heating was rather interesting. When the temperature was raised rapidly to 250–260° it melted with effervescence, then resolidified, and then could not be remelted at 340°, before which point was reached, however, con-

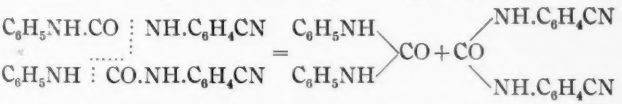
siderable darkening occurred. The effervescence of the substance at 260° was due to the splitting off of carbanilide, which boils at this temperature (260°). The carbanilide collected in the upper part of the melting-point tube as a crystalline sublimate.

To ascertain the nature of the substance remaining after the separation of carbanilide, a larger portion of the phenyluraminoquinazoline was heated at 270–280° until all carbanilide was removed. The residue was boiled with water and then with alcohol. The material left undissolved by this treatment could not be crystallized, as it was not appreciably soluble in any of the ordinary solvents. It did dissolve in warm dilute potassium hydroxide solution, but when reprecipitated from such a solution by dilute acids or by carbon dioxide separated in a jelly-like condition. It was decomposed by boiling with concentrated caustic alkalies. Judging from previous experience with such compounds, this insoluble substance is probably the symmetrical diquinazolylurea,

the reaction by which it is formed being as follows:



Such a reaction corresponds entirely to the formation of carbanilide and di-*m*-cyancarbanilide by heating *m*-cyancarbanilide:[1]



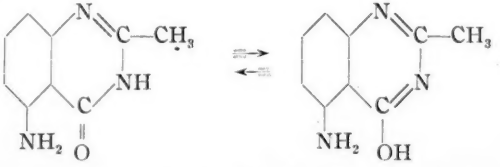
In further support of the above deduction, the aminoquinazo-

[1] Bogert and Beans: This Journal, 26, 466 (1904).

line was dissolved in pyridine and carefully treated with a 20 per cent. solution of phosgene in toluene. After the first vigorous reaction was over, the mixture was heated for a few minutes, then poured into water, dilute acetic acid added to acid reaction, and the undissolved material filtered out. This insoluble portion showed exactly the same behavior as the product obtained by heating the phenyluraminoquinazoline above 260°. On account of the great insolubility of the substance, it has not been possible to get it in a condition that we could regard as sufficiently pure for analysis.

Other Reactions of 5-Amino-4-ketodihydroquinazoline.—Besides the above, the aminoquinazoline gave other typical aniline reactions. With chloroform and potassium hydroxide solution, an isonitrile odor was developed. With benzaldehyde, an insoluble condensation product was obtained, presumably the benzylidene derivative. With nitrous acid, a diazonium body was produced, and also a nitroso derivative. The presence of the former was demonstrated by coupling the diazotized quinazoline with β-naphthol, when a reddish-brown dyestuff resulted; while the nitroso group was detected by the Liebermann reaction. These reactions indicate the presence of both the primary amino group (in the benzene cycle) and the secondary imino group (in the miazine cycle).

5-Amino-2-methyl-4-ketodihydroquinazoline (*5-Amino-2-methyl-4-oxyquinazoline*).



—5-Nitro-2-methyl-4-ketodihydroquinazoline was reduced with stannous chloride and hydrochloric acid in the manner already described for the 5-amino-4-ketodihydroquinazoline, but the separation of the reduction product was much more troublesome, on account of its insolubility in hot water. At the conclusion of the reduction, the mass was made alkaline with sodium carbonate, boiled for a short time, allowed to cool, and filtered. The material thus filtered out was dried in the air, extracted repeatedly with

boiling alcohol or boiling ethyl acetate, the extracts combined, concentrated, and the concentrated solution allowed to cool. Pale, reddish-brown needles of the aminoquinazoline separated, in poor yield.

Calculated for $C_9H_9ON_3$: N, 24.0. Found: N, 24.0.

This aminoquinazoline melts with decomposition at 295–310°. It slowly darkens in the light. It is moderately soluble in alcohol, acetone or ethyl acetate, when boiling, less so when cold, and is practically insoluble in cold water, benzene or ether. In dilute caustic alkalies, it dissolves readily, and is reprecipitated from such solutions by carbon dioxide or by dilute acids. It is also soluble in strong hydrochloric acid.

Hydrochloride.—Dry hydrogen chloride, passed into an ethyl acetate solution of the aminoquinazoline, caused the separation of the hydrochloride as a nearly white crystalline precipitate. This salt is dissociated when boiled with plenty of water.

Chlorplatinate.—The hydrochloride was dissolved in a small amount of dilute hydrochloric acid, and treated with a solution of chlorplatinic acid. The chlorplatinate separated at once as a crystalline precipitate.

Calculated for $(C_9H_9ON_3.HCl)_2PtCl_4$: Pt, 25.66. Found: Pt, 25.56.

HAVEMEYER LABORATORIES, COLUMBIA UNIVERSITY,
December, 1905.

[CONTRIBUTION FROM THE TEXAS EXPERIMENT STATION.]

NITRIFICATION AND AMMONIFICATION OF SOME FERTILIZERS.

BY G. S. FRAPS.

Received October 31, 1905.

IN 1901, Withers and Fraps found[1] that in a certain soil, the amount of nitrates produced from organic materials was in the order of their availability as measured by vegetation tests and solubility in potassium permanganate. A later study by the same authors[2] showed that this relation does not hold for all soils, but the rank of the fertilizer, if measured by nitrates formed under similar conditions, varied with different soils. Placing

[1] This Journal, **23**, 318 (1901).

[2] Report for the N. C. Experiment Station for 1902–'03, p. 31.

the nitrogen oxidized from cotton-seed meal as 100, the rank of the others varied in five soils as follows:

Ammonium sulphate	13 to 127
Dried blood	70 " 120
Fish	85 " 190
Bone	22 " 43

Plants, however, can assimilate not only nitrates, but also ammonium salts, and certain organic nitrogenous bodies, such as tyrosin, urea, etc. Consideration of this fact leads to the determination of the ammonia formed as well as nitrates.

The further study of the nitrification and ammonification of organic materials to be described in this paper, has not only given some explanation for the variations noted above, but also justifies the following statement: While the relative amounts of nitrates produced from different materials in different soils under comparable conditions depend largely upon the nature of the soil, the production of ammoniacal plus nitric nitrogen depends almost entirely upon the nature of the material.

METHOD OF WORK.

It is known[1] that soils vary widely in "nitrifying power," that is, ability to serve as mediums for the growth and development of nitrifying organisms. For the purpose of this investigation, three soils were selected which differed considerably in nitrifying power:

Soil 75 was a poor white sand from Nacogdoches, Texas, low in nitrifying power, and of low water capacity.

Soil 77 was a brown clay loam from College Station, Texas, of medium nitrifying power, good water capacity and responding well to applications of phosphoric acid.

Soil 131 was a brown soil termed Orangeberg, a fine sandy loam, from Elmendorf, Texas.

The nitrification tests were conducted as follows: Five hundred grams of dry soil were mixed with 20 grams nitrifying earth, soil from a field, which was moist and contained the nitrifying organism, an amount of nitrogenous substance containing 0.3 gram of nitrogen, and water equal to one-third of the saturation capacity of the soil. The nitrogenous substance and nitrifying earth were first mixed, then these were incorporated with the dry soil, the water added, and the whole mixed thoroughly until the mass was

[1] Am. Ch. J. 29, 225 (1903).

uniform. The mixture was placed in 500 cc. precipitating jars, shaking it down by tapping gently against a wooden block, or by the hand. A test-tube with a small perforation in the end was inserted to the depth of about an inch, the jar and its contents weighed, and placed in a water-bath kept as nearly as possible at 35° C. The most satisfactory method of marking the jar with its weight and number is by means of a pencil on a rough surface etched with diamond ink. Every Monday, Wednesday and Friday, each jar was placed on a coarse balance, and water added through the test-tube until its original weight was restored.

After four weeks the contents of the jars were mixed thoroughly. One hundred grams were placed in a funnel on a perforated porcelain disk, and washed with water until the volume of the filtrate was about 100 cc. Nitrates were then determined in the filtrate by the Tiemann-Schulze method, and calculated to the original weight of the mixture.

For the ammonia determination, an amount equal to 200 grams of the dry soil was placed in a flask with dilute hydrochloric acid (1:25) in quantity sufficient to make 500 cc. with the water contained in the sample. The mixture of soil and acid was shaken thoroughly, filtered after standing over night, and 250 cc. of the filtrate distilled with magnesia. The ammonia was caught in standard acid and the solution titrated back with ammonia. Correction was made for ammonia in the reagents. Both nitric and ammoniacal nitrogen were corrected for the quantity present in the original soil.

Both determinations were made in duplicate jars; as a rule the nitrate determinations agreed very well, while the ammonia determinations were less satisfactory.

RESULTS OF NITRIFICATION.

The nitric nitrogen produced, in percentage of total nitrogen added in the fertilizer, and the relative value of the materials on this basis, are presented in Table I. The results are similar to those in the paper of Withers and Fraps already referred to; namely, that the rank of the fertilizers measured by the relative amounts of nitrates produced from them varies according to the nature of the soil.

These variations are apparently due, in large part, to other

fertilizing constituents carried by the materials. From unpublished work of the author it appears that acid phosphate, potassium sulphate, or calcium sulphate, one or more, may sometimes have a decided effect upon nitrification on many soils, and a low nitrifying power may sometimes be due to deficiency in plant food for the nitrifying organisms. Ammonification is decidedly less sensitive. Referring to Table I, we

TABLE I.—NITRIFICATION OF FERTILIZERS.

	Percentage of added nitrogen oxidized to nitrates.			Rank.		
Material.	In soil 75.	In soil 77.	In soil 131.	In soil 75.	In soil 77.	In soil 131.
Cottonseed meal.....	8.2	20.3	7.6	100	100	100
Blood.....	6.6	23.1	5.9	80	114	79
Bone.....	18.6	17.6	21.9	227	87	288
Bat guano.....	17.5	17.8	22.0	213	87	289
Cow manure.....	lost	9.9	8.9	lost	49	117

find that the high rank of bone and bat guano in soils 75 and 131, and of cow manure in soil 131, is not due so much to increased nitrification of these materials, as to decreased nitrification of cotton-seed meal and blood. A close comparison is not permissible, since the initial number and activity of the organisms in each series was probably not exactly the same.[1] The decreased nitrification of the cotton-seed meal and blood in the two soils was probably due to deficiency in phosphoric acid in the soil, which is carried by the bone and bat guano in large quantity; and indeed by cotton-seed meal also, though not in sufficient amount. This explanation of the difference in nitrification in the soils is in accordance with the effect of the different materials in soil 131, as follows:

	Percentage of added nitrogen oxidized to nitrates.
No addition.....	14.1
Calcium carbonate.....	29.6
Potassium sulphate.....	20.1
Acid phosphate.....	21.0
Calcium carbonate and acid phosphate.....	34.6

From this it would appear that some soils are sometimes deficient in phosphoric acid and potash for the nitrifying organisms, and fertilization with these ingredients may increase nitrification.

AMMONIFICATION AND NITRIFICATION.

The sum of the ammoniacal and nitric nitrogen from the different materials, expressed in terms of the total nitrogen applied,

[1] See Fraps: Am. Ch. J. 29, 225 (1903).

is given in Table II, and also the relative values of the fertilizers on this basis. Some variations are to be found, as can be expected, but they are moderate and by no means as great as with the nitrates taken alone. They are probably due to differences in the nature of the soil. The relative amounts of nitric plus ammonia nitrogen depend most largely upon the nature of the material, and are in the order of the availability of the fertilizer.

TABLE II.—NITRIFICATION AND AMMONIFICATION.

	Percentage of nitrogen converted into nitrates and ammonia.			Rank.		
Material.	In soil 75.	In soil 77.	In soil 131.	In soil 75.	In soil 77.	In soil 131.
Cottonseed meal.....	51.5	39.4	49.3	100	100	100
Blood.....	56.4	43.9	42.9	110	111	86
Bone.....	20.7	23.9	23.7	40	61	47
Bat guano.....	29.1	24.8	33.5	57	63	67
Cow manure.....		9.6	8.3	.....	24	17

An obvious inference from this statement is that the ammonifying group of organisms is apparently not as sensitive to the condition of the plant food in the soil as the nitrifying organisms, perhaps having greater power of securing it. This inference appears justified from work on the effect of various additions to the soil upon nitrification and ammonia production.

The absolute amount of nitrates and ammonia formed would probably depend upon the number and activity of the organisms with which the soil was inoculated at the beginning of the experiment, as well as on the nature of the material and the conditions of the experiment. Forty-three to 56 per cent. of the nitrogen of dried blood was changed into ammonia and nitrates in four weeks under the conditions of these experiments. This is considerably less than 73 per cent., which is probably the average value for the availability of blood compared with sodium nitrate as 100 in vegetation experiments. With a longer period of time for nitrification, more of the nitrogen would be converted into nitrates and ammonia.

RATE OF TRANSFORMATION.

The nitrogen recovered as ammonia and nitrates in our tests represents the more readily available nitrogen of the material, or that which is most easily attacked by bacteria. The transformation will continue at a decreasing rate, until it will become so slow as to be practically indistinguishable from the change of the soil nitrogen.

We have determined the rate of production of nitric and ammonia nitrogen in soil 77. A set of 10 jars was prepared under the same conditions, and kept in the constant temperature bath. Every week two jars were removed for the determination of nitrates and ammonia. Correction was made for the original content of nitrates and ammonia. The results (average of duplicates) are presented in Table III.

TABLE III.—RATE OF CHANGE FOR THE NITROGEN OF COTTONSEED MEAL.

Time in days.	Percentage of nitrogen converted during each period into nitrates.	ammonia.	total.
7	−0.4	+22.2	+21.8
15	+7.0	+ 4.1	+11.6
21	+8.8	− 4.1	+ 4.7
28	+7.8	− 5.7	+ 2.1
35	+3.5	+ 2.2	+ 5.7
42	+0.8	− 0.9	− 0.1
49	+1.0	− 4.8[1]	− 3.8
56	+1.2	+ 3.6	+ 4.8
Total.....	29.7	16.6	46.3

[1] This is perhaps an error.

Nitrification begins the second week, and reaches its maximum during the third, and decreases to the sixth week, after which the rate increases slightly; that is to say, the nitrification is periodic, as pointed out in a previous article. The total change (sum of nitric and ammoniacal nitrogen) is greatest during the first week, and decreases to the fourth, after which it is somewhat irregular. The ammonia formation has its maximum during the first week, and is positive during the second, after which it is for the most part negative, owing to change into nitrates. However, the ammonia formation goes on during almost all the periods, since the total change is positive in every period save two, although we must also consider the possibility of direct conversion of organic nitrogen into nitrates, without passing through the intermediate ammonia stage. There is evidence in favor of the view that such a direct change takes place.

At the end of fifty-six days, the nitrogen of the cottonseed meal was distributed as follows:

	Per cent.
In nitrates.....	29.7
In ammonium salts.....	16.6
In other forms	53.7

COMPARATIVE VALUE OF AMMONIA AND NITRATES.

The facts presented in this paper lead us to the opinion that the ammonia nitrogen of the soil is of more importance than is generally held to be the case. The statement that nitric nitrogen is the only form in which nitrogen is assimilated by cultivated plants has been noted several times lately.[1] There is evidence that plants are able to assimilate ammonia, and some organic bodies such as asparagin, glycocoll and urea in addition to nitrates, leaving out of consideration the assimilation of atmospheric nitrogen by leguminous plants in symbiosis with bacteria. While nitrates are usually more abundant in cultivated soils than ammonia, yet the ammonia is present, and being present may be assimilated. In rice-growing, when the soils are saturated with water during most of the growing season, and in some compact soils, where physical condition is little favorable to nitrification, nitrates cannot play a great rôle in the nutrition of the plants.

The experiments here described have shown that at the end of four and even eight weeks, under conditions favorable for nitrification, a large portion of the nitrogen rendered assimilable to plants by changes in the soil is often present as ammonia (see Table IV). This proportion will of course decrease with time,

TABLE IV.—AMMONIACAL NITROGEN IN 100 PARTS NITRIC AND AMMONIACAL NITROGEN.

Soil.	75.	77.	131.
Cottonseed meal	84	49	85
Blood	88	47	89
Bone	10	26	8
Bat guano	40	29	34
Cow manure	lost	0	0

but the nitrification is slow after four weeks. Such being the case, it is obvious that ammonia must play a not insignificant part in plant nutrition when fertilizers or manures are applied. It may be objected that the ratio of soil to fertilizer is smaller than in practice, and with the same quantity of material in a larger quantity of soil, nitrification will take place more rapidly.

[1] C. G. Hopkins: Bulletin 94, Ill. Expt. Station, page 1; Chester: Bulletin 40, Del. Expt. Station; Patterson: Bulletin 91, Md. Expt. Station, page 28; Stubbs: Bulletin 77, La. Expt. Station; Harris: "Food for Plants," p. 6; F. H. King: "Year Book," U. S. Dept. of Agric. 1903, p. 170.

This objection must be considered, but we must remember that in the field the fertilizer is not mixed intimately with all the soil to the depth of twelve or six or four inches, but is distributed in the row or broadcast, often in a lumpy condition, and comes in direct contact with only a limited quantity of the soil to which it is applied.

If plants depend entirely upon nitrates for nitrogen, the fertility of a soil should depend largely upon its ability to support the nitrifying organisms, and the availability of organic fertilizers would vary with the nitrifying power of the soil to which they are applied. If both ammoniacal and nitric nitrogen were assimilated with equal readiness by plants, the fertility of the soil would bear little relation to its nitrifying power, since the production of ammonia seems to depend more on the material than on the soil. Nitric and ammoniacal nitrogen are probably of unequal value, varying with the nature of the plant. In most cases the nitric nitrogen is probably more easily absorbed than ammonia; the nitrifying power of a soil must therefore be of some influence upon its fertility, though not so great as if ammonia were totally unavailable.

Unfortunately, we have no quantitative determination of the availability of ammoniacal compared with nitric nitrogen under conditions excluding nitrification of the ammonia. In pot and field tests, in which more or less of the ammonia is nitrified, ammonium salts as a rule are not equal to nitrates. The difference has been ascribed to the beneficial effect of the sodium of the sodium nitrate,[1] or to the injurious effect of the acid residue of ammonium sulphate, but it may also be due to the incomplete nitrification of ammonia, and the lower capacity of the latter to serve as nourishment for the plants under study. Wagner[2] assigns the value 90 to the nitrogen of ammonium salts, compared with sodium nitrate nitrogen as 100. Wheeler[3] found nitrogen in ammonium sulphate to have the value 92.2 on a limed soil, less than nothing on the unlimed acid soil, with nitric nitrogen equals 100 as the standard.

[1] P. Wagner: "Die Stickstoffdüngung der landwirtschaftl. Kulturpflanzen, 1892."

[2] Loc. cit. Later he gives a value of 94 as an average for all pot experiments. Ausführung v. Felddüngungsversuchen, 1904.

[3] Rhode Island Bulletin, No. 53.

It seems probable that ammonia nitrogen, as such, has a lower value for most cultivated plants than nitric nitrogen. Such being the case, the nitrifying power of a soil must have some influence upon the crop value of the fertilizer nitrogen placed in it.

DETERMINATION OF AVAILABILITY OF NITROGEN.

Vegetation tests for comparing the values of nitrogen in different forms are influenced by a number of variables, as the nature of the soil, the kind of plant, the season and the effect of the fertilizer on succeeding crops, all of which must enter into consideration. The results of different individual experiments vary considerably. Thus for the nitrogen of blood, compared with that of sodium nitrate as 100, we have the figures 76, 68, 73, 95, 58, 61, 85, 69, 68, 73, 73, 83, 51,[1] as values in separate experiments by several workers. The average of several series of experiments may agree better. Thus Jenkins and Britton's average for three years was 73, Wagner's average is 69, von Sigmond's 67, Pfeiffer, Franke, et al., is 85.

As regards the effect of the soil, Wheeler found the availability of the nitrogen of dried blood to be 45.5 in an unlimed acid soil, 90.3 in the same soil limed, compared with sodium nitrate nitrogen as 100, while ammonium sulphate had the availability of less than zero in the acid soil, 92.2 in the limed soil.

Availability will also depend to a certain extent upon whether one or several crops is taken up for the measurement. Quick-acting fertilizers will appear comparatively more available with one crop than with several, in which the slower have greater chance to show results.

It will be concluded that the amount of assimilable nitrogen that can be produced from a given substance is a measure of its availability. It is not the fault of the material if the soil conditions are such that the maximum of assimilable bodies is not produced, or, being produced, if the plant is unable to take them up, because they are washed out, fixed, or for other reasons.

To compare organic materials with sodium nitrate directly, it would be necessary to select such a period of time and such

[1] Experiment Station Record, **7**, 193; **8**, 387; **9**, 541; **10**, 233; **12**, 323; **13**, 323; **11**, 134; **14**, 557; **15**, 235, 660. Jenkins and Britton: Experiment Station Record, **10**, 233. Wagner average: Ibid. **11**, 134. Von Sigsmond average: Ibid. **15**, 660. Pfeffer, Franke, et al., Ibid. **11**, 134.

conditions, that the substance would be converted into as much assimilable compounds as it would be during the growing season of the plant. According as the time selected is longer or shorter and the number and activity of the soil organisms used to inoculate the soil increase or diminish, different results would be obtained. The comparison of organic materials directly with sodium nitrate is thus subject to serious difficulties.

The comparison of different organic materials does not offer such difficulties, and it is believed that the method, as pointed out in this paper, will be of value for this purpose. It can neither supplant vegetation tests, nor take the place of a rapid chemical method for determining availability, but in its own sphere should be of value. The work in this paper has been confined to the amount of nitric and ammonia nitrogen formed; as has been stated, some organic compounds may be assimilated directly by the plants, but the determination of the amounts of such of these as are formed in the decomposition of organic matter in the soil, offers grave analytical difficulties.

SUMMARY.

(1) Nitrogenous fertilizers may be divided into two classes: those which are compounds directly assimilable by plants, and those which must first be converted into assimilable bodies before the nitrogen is of value.

(2) The rank of fertilizers measured by the relative amount of nitrates produced from them depends upon the nature of the soil.

(3) These variations depend sometimes upon the need of the soils for the other fertilizing ingredients carried by the material.

(4) The relative amounts of nitric and ammoniacal nitrogen produced from different material under similar conditions depend most largely upon the nature of the materials, and is in the order of their availability. The soil is, however, of some effect.

(5) The ammonifying group of organisms is not so sensitive to the condition of plant food in the soil as the nitrifying organisms.

(6) In an experiment to test the rate of formation of nitrates and ammonia, ammonia was formed most rapidly during the first week, and is positive during the second, after which it is for

the most part negative, owing to conversion into nitrates. Nitrification begins the second week, reaches its maximum during the third week, then decreases; that is, it is periodic. The total change is greatest during the first week, and decreases to the fourth, after which it is somewhat irregular.

(7) Since a large part of the nitrogen rendered available is in the form of ammonia, it is probable that ammonia plays a greater part in plant nutrition than is commonly assumed to be the case.

(8) Ammonia is probably of less value than nitrates for most cultivated plants, and the nitrification power of soils is of importance.

(9) Determination of the relative amounts of nitric and ammonia nitrogen produced from them should be of value in comparing different organic materials.

[Contribution from the Committee on Uniformity in Technical Analysis. II.]

COOPERATIVE ANALYSIS OF AN ARGILLACEOUS LIMESTONE.

Received December 30, 1905.

Introduction.

The present contribution deals with the results obtained in an effort of the committee to secure information of the nature indicated in the second paragraph of the list of its aims as published in this Journal **26,** 1652. In other words, to endeavor to ascertain if a part of the blame for the notorious inability of different analysts to report closely agreeing results when analyzing the same materials is to be placed upon the instructors in analytical chemistry in our higher institutions of learning. The subject is, of course, a difficult one to handle, but it was hoped that by a frank invitation to coöperate a sufficient number of public-spirited instructors, earnestly desirous of improving a plainly serious situation, might be secured to afford some positive indication one way or the other.

To this end a circular letter was addressed on Jan. 1, 1905, to the heads of the chemical departments in nearly 100 universities, colleges, polytechnics and mining schools throughout this country and Canada. It was proposed to send to all who might be willing to have an analysis or analyses made by their instructors or advanced

students a portion of a carefully prepared, large sample of argillaceous limestone, with a view to testing the skill of the instructors as analysts and their ability to impart skill to those in their charge. About 70 replies were received, only two of which were refusals to coöperate. Many of the letters received were extremely favorable to the purpose of the committee, and some pledged the writers to faithful coöperation.

About the middle of February samples were sent to all who had expressed a willingness to coöperate, accompanied by a second circular letter specifying the nature of the analysis desired. This "should be of such a character as to illustrate the methods used in your institution for teaching general quantitative analysis without technical application....." and "should be fairly representative of careful work." It was asked that all of the following data should be furnished, if possible: SiO_2, Al_2O_3, total iron as Fe_2O_3, TiO_2, P_2O_5, CaO, MgO, K_2O, Na_2O, H_2O both below and above 100°, CO_2, and total sulphur reported as S. The last might be reported as both S and SO_3, if found to exist in the sulphide and sulphate condition. The carbon of any organic matter that might be present should be reported as carbon, though this determination was not insisted on. Because of the impossibility of determining ferrous iron with any approach to accuracy in presence of organic matter, it was directed that this constituent should only be reported in case carbonaceous matter and sulphides were absent. And because the iron might exist in the two states of oxidation as well as in the sulphide state, and their distinct determination be probably impossible, it was thought best to ask that all be reported as Fe_2O_3, even though it was probable that most of it existed in the ferrous condition as carbonate, a very common condition in limestones. It was fully understood that the values reported for water above 100° would include that due to oxidation of the hydrogen of any carbonaceous matter that might be present, and not solely that from the silicates, but this was of no moment, since it was the ability to determine water correctly that was in question and not the distribution of this water among the mineral constituents of the sample. It will be seen that the determination of some of these points would offer a slight field for the qualitative determinative skill of the analysts.

It may be said here that these directions were but indifferently

observed by many of those who sent in reports. By some they were totally disregarded, with the result, for instance, that, only sulphate sulphur being looked for and little or none found, sulphur was reported to be absent, whereas it was present in some quantity in its usual sulphide form. Again, there is reason to believe that in some instances the total was reported as SO_3, without any attempt having been made to determine its actual condition. Still again, many made no mention of titanium or phosphorus yet reported figures for alumina which included one or both of those elements as TiO_2 and P_2O_5. In another case the work of students without previous experience in quantitative work was reported. And lastly, technical methods were occasionally reported, showing disregard of the directions or else an implication that none but technical methods were taught in the institution.

THE SAMPLE.

The sample of limestone was prepared and furnished by Mr. H. A. Schaffer, of the Northampton Portland Cement Company, Stockertown, Pa., to whom the thanks of the committee are cordially rendered. It weighed about 200 pounds and was expected to wholly pass a 200-mesh sieve, but mechanical difficulties did not allow of this degree of fineness being reached by quite all of the powder. It was found that about 94 per cent. passed the sieve. The remainder differed somewhat in composition from that which passed through, as shown by comparing the following determinations with the corresponding ones of the bulk analysis at the head of the table below: SiO_2, 17.48; Al_2O_3, etc., 7.84; CaO, 38.54; MgO, 2.12 (incl. Mn and a trace CaO). It is considered in the highest degree improbable, however, that any detectable amount of segregation could happen during transport or storage of such fine material, whereby variations in the small samples might arise.

In order to learn if the sample was homogeneous throughout, six small lots were taken at intervals from top to bottom of the barrel and silica was determined in each by the chairman of the committee, this being a determination susceptible of very great accuracy when properly carried out. The results were 18.09, 18.10, 18.10, 18.05, 18.11, 18.14, thus showing complete homogeneity.

THE STANDARD ANALYSES.

Careful analyses to serve as standards of comparison were made by the chairman of the committee in the laboratory of the U. S. Geological Survey and by Dr. C. E. Waters at the Standards Bureau. The results, given at the head of the table below, are in each case the mean of closely agreeing determinations. The two analyses are sufficiently alike to serve satisfactorily the purpose for which they were made. Not much needs to be said regarding the methods used by the two analysts. They were in the main those laid down in Bulletin 176 of the Geological Survey. The ratio of silica to carbonate minerals is such that strong ignition would not give a product wholly soluble in hydrochloric acid, an observation made by some of the other analysts also, hence fusion with a small amount of sodium carbonate was resorted to in order to afford complete solubility in hydrochloric acid. Manganese was determined by the colorimetric method with ammonium persulphate and a silver salt. The carbon of carbonaceous matter was determined at the Standards Bureau by oxidation with chromic acid, and at the Survey by combustion in an air current after extraction of the carbonates by dilute hydrochloric acid and filtering on asbestos. The CO_2 evolved was in both cases weighed. It may be that this method is open to the objection that some of the carbonaceous matter may have been volatilized by the preliminary acid treatment. It is, however, certain that any loss from this cause is insignificant. In any case the values reported are not too high. The analyst of the Standards Bureau determined strontia and ignition loss and also noticed the evolution, on heating, of a small amount of ammonium salts. The Survey analyst made no effort to discover other components than those called for by the circular letter above referred to, but he did determine ignition loss, since this was done by most of the technical analysts. For the general correctness of the standard analyses, the ignition losses shown in them bear very strong evidence. This loss should cover (CO_2 + C + all H_2O) — (the gain by oxidation of FeS_2 to Fe_2O_3 and SO_3 + the gain of all the rest of the iron from FeO to Fe_2O_3), for it is safe to assume that all iron not pyritic in this case is in the ferrous state. At the temperature employed by the Survey analyst, all the sulphur is retained as sulphate by the lime, the carbonate is completely decomposed, and there is no loss of alkali.

On this basis the calculated loss in his analysis should have been 32.26 per cent. Duplicate tests on 1 gram and 0.5 gram respectively gave 32.25 and 32.23 per cent. For his method, see this Journal, **25,** 1198 and 1199. Similar computation for the analysis from the Bureau of Standards shows a calculated loss of 32.43 against one of 32.30 found. The difference in the two calculated losses is just equal to the difference in the respective CO_2 percentages.

THE COOPERATIVE ANALYSES.

Of the sixty-eight educators who expressed willingness to aid by furnishing analyses if possible, only a small proportion have reported at the date of completion of this report, or twenty-five in all. Many excused themselves for reasons of a varied character, and sixteen have not been heard from, notwithstanding a third circular letter calling attention to the neglect. A few hoped still to be able to report and may yet do so. The returns are therefore too limited in number to afford safe grounds for final general conclusions, except in a few particulars. It does not seem wise, however, to defer issuing this report, especially since a large number of chemists in technical work who applied for samples of the limestone are naturally desirous of comparing the standard analyses with their own. It is to be said regarding the collegiate analyses that they are from thoroughly representative institutions covering the United States from the extreme east to the Pacific coast and from the northern boundary to the Mexican line. Canada is not represented.

The committee refrained from soliciting comparative analyses from technical laboratories, for this ground has been fairly covered by the reports of other committees. Nevertheless it is glad to include in the tabulation below the few analyses received from these laboratories and to express its pleasure at the interest displayed by all, and appreciation of the intelligent description and discussion, by two or three, of their methods and results.

The analyses are tabulated in three classes, according as they are the work of instructors, advanced students or technical chemists. Six analyses by beginners in one institution have been omitted. Seventeen instructors from as many institutions are represented by analyses, and fourteen students from eight institutions, only two of these last being represented also by

instructors. In this respect analyses 9 and 18 *a*, *b*, *c*, belong together, as also 5 and 23.

Before discussing the analyses, a few explanations are in order, so that those who find changes in their figures may understand why they were made. (1) It was requested that the analyses be calculated on the dried material, but that the hygroscopic moisture be reported separately. Most, however, included the moisture in the summations, and it was decided to follow this plan throughout, so far as possible. The change necessitated the recalculation of a few analyses. In one case, owing to failure to report the moisture, the air-dry analysis has been recalculated on the assumption of the average moisture content shown by the other coöperative analyses. (2) When, as occurred among the technical analyses, lime and magnesia were reported as carbonates, the bases have been calculated for the table, but the CO_2 ignored as not based on direct experiment. (3) When more than one analysis by the same person was reported, only the averages are given in the table, except as determinations may have been made by different methods. (4) In three or four instances among the technical analyses "ignition loss" was referred to dry material. For the sake of uniformity it has been increased in such cases by the amount of moisture reported. (5) Most of the analyses were incomplete, and many recalculations were called for as indicated above, hence totals have been omitted for all but the standard analyses and one other.

After careful consideration it has been deemed best to make public no names, either of analysts or of their respective institutions. It is hoped that the committee will not be considered lacking in courtesy on account of this decision. It takes this occasion to thank most heartily one and all who have contributed material for this presentation.

DISCUSSION OF ANALYSES.

Space does not permit of detailed discussion of the varying causes that have contributed to erroneous results in individual cases, even where these are apparent from inspection of the analyses or of the reported methods. Some of the analysts have expressed a desire, however, for criticism or comment on their work. This the chairman holds himself ready to give to the best of his ability by letter, and he cordially invites correspond-

TABLE OF ANALYSES (averages only given where duplicates were reported).

Analyst.	SiO_2.	TiO_2.	Al_2O_3.	P_2O_5.	Fe_2O_3.	MnO.	CaO (SrO).	MgO.	K_2O.	Na_2O.	H_2O 105°—.	H_2O 105°+.	S.	SO_3.	CO_2.	C.	Total.	Ign.	Remarks.
Hillebrand	18.11	0.23	5.78	0.18	1.75	0.04	37.68	1.96	1.17	0.36	0.16	1.48	0.26	0.015	30.59	0.66	100.26[1]	32.24	0.09 SrO incl. in the CaO by Bur. Stands.
Waters	18.18	0.21	5.62	0.18	1.68	0.04	37.62	1.91	1.12	0.30	0.15	1.53	0.28	0.010	30.77	0.63	100.05[1]	32.30	
Instructors.																			
1	17.98	0.22	5.91	0.21	1.76	n.d.	38.11	2.03	1.21	0.66	0.11	0.65	0.33		30.77	0.70			
2	17.42	0.23	6.72	0.19	1.86	0.15 0.06	37.55	2.06	1.19	0.51	0.08		0.26		28.65	1.58			Higher MnO grav., lower MnO by color. C = "humus."
3	17.46	0.11	5.87	0.19	2.70	none		2.42	1.25	0.72	0.27	1.69	0.29						
4	17.90	0.17	7.35	0.18	1.54		37.83	2.03			0.08							32.38	
5	17.95	0.35	5.73	0.12	1.76	0.07	37.89	2.05	1.15	0.29	0.14	1.53[2]	0.29		30.46			32.52	MnO "probably low." CaO includes Mn_2O_3.
6[3]	17.86	0.20	7.14	0.17	1.14	0.06	37.64	2.09	1.09	0.32	0.08								MnO by colorimetry.
7	17.16	0.56	5.10	0.17	1.56	0.27	39.53	2.12	1.22	0.40	0.11			0.33				31.94	"Complete analysis."
7a	17.35	5.79		0.17	1.57		39.83	2.20											"Technical analysis."
8	17.72 18.16	5.05		0.65	2.51	1.70	38.08	2.11	1.48	1.85			none						Silica by two methods. Alkalies "probably high."
9	18.05	5.83		0.20	1.94	trace	37.95	2.11	1.33	0.58	0.11	1.32	trace	none	30.41	n.d.			
10	18.92	6.12		0.17	1.64		37.24	2.06	n.d.	n.d.			0.28		30.93	n.d.			
11[3]	17.77	9.51		0.36	2.41	trace	37.83	2.01	1.03	2.00	0.17				30.52	1.92	(105.53)		C = "Carbonaceous matter."
12	18.07	6.76			1.72		37.88	1.89	0.94	0.67	0.05		0.29		30.65				Commercial methods used, avoiding large errors.
13	17.72	6.38			1.82		37.42	2.19											

[1] Totals corrected for the fact that pyritic iron counts in the analysis as Fe_2O_3 instead of Fe. The totals are still high by about 0.16 per cent., for the reason that most, if not all, of the residual iron should be counted as FeO instead of Fe_2O_3.

[2] Average of five determinations between the limits 1.27 and 1.78.

[3] Separate analyses made of parts soluble and insoluble in hydrochloric acid (see p. 236). These have been combined for the table.

TABLE OF ANALYSES (averages only given where duplicates were reported)—*Continued.*

Analyst.	SiO_2.	TiO_2.	Al_2O_3.	P_2O_5.	Fe_2O_3.	MnO.	CaO (SrO).	MgO.	K_2O.	Na_2O.	H_2O $100^{0}-$.	H_2O $100^{0}+$.	S.	SO_3.	CO_2.	C.	Total.	Ign.	Remarks.
14	17.99		7.32		1.81		38.23	2.06	1.38	0.25	(0.12)	1.02	0.42		30.32				No moisture reported. Analysis recalc. to undried material.
15	17.79		7.15		0.82		37.68	2.12	1.16	0.47	0.16	1.21	0.29		30.68				Al_2O_3 includes "MnO_2."
16	17.21			12.29		trace	38.00	1.31		traces		0.12			30.54				Sample treated as a clay in 17, but in 17*a* extracted by HCl, residue fused, solutions combined. Same analyst. C = "organic matter."
17	18.03			8.55			36.74	3.05	1.35	0.60	0.06				29.64	1.44			
17*a*	17.94			8.02			36.02	2.14											
								Students.											
18*a*	17.88		5.61		0.27	1.94		37.64	1.79	1.61	0.93	0.20			30.52				Undergraduates at same institution.
18*b*	17.73		5.81		0.34	2.09		37.77	2.29	1.93	0.81	0.26			30.62				
18*c*										1.46	0.82				30.34				
19	17.67		4.80		0.22	2.83[1]	none	35.26	5.20	1.77	0.04	none	0.30	none	31.65				Graduate student.
20	16.40			10.16				41.98	1.58			0.19				4.72			Grad. stud. (?). C = "organic matter."
21	17.05	0.22	4.42	0.29	2.02	trace	37.80	2.04	1.62	1.51	0.10	0.03	0.34		31.27	1.55		32.82	Grad. stud. C = "carbonaceous matter."
22*a*	18.40	0.22	7.57	0.64	1.91		38.03	1.66	0.46	0.11	0.14			0.50	29.17	0.41			Advanced students at same institution.
22*b*	18.85	0.20	5.98	0.48	1.90		38.32	0.92							29.78				
23	17.79										0.26				30.00				Advanced students at same institution. Small amounts of SrO, ZrO_2 and NiO reported by one or another.
24*a*	18.03	trace	6.19	0.25	2.05[1]	1.15	37.71	1.78	1.25	0.87	0.09	0.98	0.36		30.48				
24*b*	18.08	trace	6.75	0.20	1.72[1]	trace	37.17	2.06	1.14	0.91	0.07	0.93	0.33		30.50				
24*c*	17.29	0.82	6.35	0.21	2.26[1]	0.37	37.54	2.18	1.21	0.79	0.11	0.69	0.34		30.43				
25*a*	18.58		6.92		1.06		36.87	2.86	0.79	0.15			0.39	trace					Students at same institution.
25*b*	18.46		7.05		1.27		36.58	3.00	0.83	0.11			0.36	none					

[1] These four analysts all determined both FeO and Fe_2O_3 with most widely differing results. Their data have been reduced to total iron as Fe_2O_3.

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TABLE OF ANALYSES (averages only given where duplicates were reported)—*Continued.*

Analyst.	SiO_2.	TiO_2.	Al_2O_3.	P_2O_5.	Fe_2O_3.	MnO.	CaO (SrO).	MgO.	K_2O.	Na_2O.	H_2O 100°—.	H_2O 100°+.	S.	SO_3.	CO_2.	C.	Total.	Ign.	Remarks.
							Technical Analysts and others.												
26	17.69		7.11		1.64		38.34	2.20											
27	17.82		6.80		1.76		38.01	2.32			0.11			0.69				32.88[3]	S calc. from SO_3 = 0.28.
28	17.30		6.41		1.91		37.77	2.09	1.02	0.39			0.71		30.20	2.03		32.22	
29	17.97		5.84		2.04		37.94	2.68						0.66				32.48	S calc. from SO_3 = 0.26.
30	17.78		6.32		1.94		37.85	1.92					0.26					32.65	
31	17.36		5.88	none	1.97		37.55	2.62		1.62		1.25	0.34		30.82	0.46[1]		32.52[3]	"Cl not more than 0.04."
32	17.88		6.81		0.18	2.10	0.06	37.40	2.25		2.18	0.11	0.38					32.20[3]	MnO reported as 0.069 Mn_2O_3.
33	18.60	0.17	6.64	0.20	1.71		37.51	1.97				0.12	0.35			n.d.		32.23[3]	Silica regarded as high by analyst.
34	17.44		8.18				37.50	2.11										32.28	CaO also 37.38 volumetrically.
35	16.58		8.85[2]				38.24	2.49				none		0.07					

[1] Recalculation of the analyst's data affords 0.35 instead of 0.46 for this value.

[2] Including 0.23 P_2O_5.

[3] The ignition loss reported did not include moisture. For better comparison with other ignition losses the moisture separately reported has been included in the tabulated value.

ence with those who may wish further information than this report affords. To certain general features shown by the analyses it will be proper to direct attention at this time. In view of the expressed objects of the investigation most attention will naturally be given to those emanating from educational institutions, and among these those furnished by instructors will attract chief attention. While several of them compare favorably with the standard analyses, and as to a number of their determinations might indeed be substituted for them, there is no one that does not reveal a weak point or points, and there are a very few concerning which no good word can be said.

Silica.—The silica determinations are almost without exception low, but the greater number of these show no greater deficiency than can be accounted for by the fact that in but one or two cases was correction made for the silica passing into the filtrate after even two evaporations and filtrations. Almost without exception this double filtration was practised, and the generally favorable result of so doing is evident when comparison is made with the earlier series of analyses of cements and cement mixtures carried out under the auspices of the committee of the New York Section of the Society of Chemical Industry. In the isolated instances where the correction referred to was made, it was without the precaution insisted on in some of the chairman's published discussions of this particular feature.[1] All the precautions required for an exact silica determination do not seem to be as yet widely known, but in time will undoubtedly be more generally understood and followed where exact work is called for.

Another source of low results, to which the chairman has before called attention and which one of the instructors independently noticed, is the sticking of the silica to the sides of the evaporating dishes and its incomplete removal therefrom. This is most likely to pass unnoticed when porcelain vessels are used, and the instructor referred to found in one case a retention of 0.88 per cent. of silica by the porcelain dish, which could not be removed by rubbing with a "policeman" but was removed by treatment with ammonia.

Alumina, Etc.—The failure to correct for soluble silica is only in small part responsible for the generally high results reported

[1] This Journal, 25, 1193, 1205, and 1206.

for alumina, as also for the collective percentages of the constituents precipitated by ammonia. Alumina being determined in practically all cases by the common method of difference, errors affecting the iron, phosphorus and titanium, where these were determined, accumulate upon this constituent. The low alumina value in analysis 8 is to be attributed to the quite abnormally high values reported for iron and phosphorus, and in 19 to that for iron.

Phosphorus.—With but two exceptions the determinations of phosphorus by instructors and technical analysts show good agreement, but the variation is great among students.

Titanium.—Although the agreement is fairly satisfactory in about half the results reported for titanium there is evidently great room for improvement. The bad results were not all obtained by gravimetric methods.

Iron.—Though many of the values for iron are good, a few are utterly bad, and the agreement is not so close among the rest as should be with a constituent susceptible of such accurate determination. Notwithstanding that considerable carbonaceous matter was evidently present, some analysts endeavored (notwithstanding the instructions to the contrary) to determine the iron present in the ferrous state, with all manner of results not listed in the table, no two agreeing even remotely. Much of the iron exists as carbonate, a little perhaps as silicate, a part as pyrite, and possibly, though not probably in this case, a further part in the ferric state. Hence it was asked that only the total iron be reported, and for the sake of convenience as Fe_2O_3.

Manganese.—Few as the determinations of this constituent are, they show the most astonishing lack of agreement and an utter failure in most cases to make an even approximately correct determination of small amounts by gravimetric methods. That such excessive amounts should be reported when but a minute quantity is present speaks badly for the observation of the analysts, for it is difficult to understand why the appearance of the precipitate obtained should not have aroused suspicion at least. The two or three determinations by colorimetry agree among themselves and differ little from the standard.

Calcium.—There is much greater uniformity among the lime values than in most of the others, and many could hardly be im-

proved upon. The causes of the very abnormal results by analysts 7, 19 and 20 are not apparent. It does not appear from the reports that gravimetric methods have yielded better results than the volumetric method. One technical analyst reports an average 0.3 per cent. higher after a single than after double precipitation, with a corresponding difference in the opposite direction in the magnesia.

Magnesium.—In view of the results of the earlier series of analyses elsewhere referred to, the returns by instructors and technical analysts show a surprising and satisfactory agreement, though in almost every case a higher value than is shown by the standard analyses. This last is in part due to failure to correct for the lime always present in the pyrophosphate, and otherwise clearly shows the general tendency towards too high results by reason of failure to carefully remove other incompletely precipitated constituents of the sample analyzed or of the glassware and reagents used.

Alkalies.—The determinations of potash show considerable variations among themselves and deviations from the standards, but with the soda the results are almost uniformly worthless, and sometimes as astounding as those for manganese. Why this should be is not clear, but it is an observation not made for the first time. Incomplete separation of lime may be the chief cause, since the Lawrence Smith method was generally used. In one or two cases the reported corrections for alkalies in the calcium carbonate used show the reagent to have been far from excellent, and it may be that in other cases a still poorer article was employed without correction. If so, however, there is revealed a lack of proper control of reagents.

Moisture.—With few if any exceptions, moisture was determined indirectly. Quite a number of the values reported agree very closely with the indirect determinations made at the Geological Survey and the Bureau of Standards (0.11–0.12). The standard values as given in the table, however, were direct weighings of the water given off in a dry atmosphere. Although the exact determination is one of little importance in low moisture samples, the results show how far short of perfect the indirect method is. As the chairman has often pointed out, the error becomes very important with high moisture samples.

Combined Water.—For combined water the results, though not numerous, are in general as bad as those for manganese and sodium, and show a great lack of knowledge regarding this determination and the temperatures to be employed for its expulsion from silicate minerals. There is also seemingly evident much ignorance that water is a constituent of some siliceous components of limestones.

Sulphur and Sulphur Trioxide.—Few if any analysts apparently determined the condition of the sulphur in the limestone. Whereas it exists almost wholly as pyrite, some reported only SO_3. A trace of sulphur was evolved as hydrogen sulphide on boiling with dilute hydrochloric acid, not the greater part, as reported by one analyst. There has evidently been much failure to exclude sulphur from reagents or flame gases, for the variations from the standard, while not strikingly great as a rule, represent nevertheless a very appreciable weight of barium sulphate.

Carbon Dioxide.—Considering the difficulty ordinarily encountered in securing reliable results, those rendered for CO_2 are surprisingly good in the greater number of cases.

Carbon from Carbonaceous Matter.—The organic matter of the limestone is almost wholly of a coaly nature, and not "humus" as thought by a few analysts. The determinations are too few in number to merit special comment, but the methods used in a few cases were extremely faulty.

Ignition Loss.—There is here, as with CO_2, a very good general agreement with the standards. It is a determination which appeals more to the technical analysts than to others, and one which by the exercise of proper and easily applied precautions will always represent a certain algebraic sum of losses and gains in all limestones not ideally pure. For further comment on this point see p. 237.

In the limits of a single table it is impossible to bring to view all the data furnished by the reports. For instance, two analysts (instructors) decomposed the limestone by hydrochloric acid and analyzed separately the soluble and insoluble portions. Comparison of the results arrived at in the two cases, in so far as the same constituents are covered, is instructive, if not in all respects gratifying.

	Insoluble in HCl.		Soluble in HCl.	
	Analyst 6.	Analyst 11.	Analyst 6.	Analyst 11.
SiO_2	17.86	17.77	....	....
Al_2O_3	5.64[1]	7.85[1]	1.84	1.66
P_2O_5		0.14		0.22
Fe_2O_3	0.43	1.29	0.71	1.12
CaO	none	0.11	37.64	37.72
MgO	0.54	0.37	1.54	1.64
K_2O	1.09[2]	0.77	none[2]	0.26
Na_2O	0.32	1.31	none	0.79
	(25.88)	(29.61)	(41.73)	(43.41)

The above affords a striking illustration of the dangers resulting in part from wrong choice and application of analytical methods, and in part from failure to ascertain beforehand the composition of the material to be analyzed. In close agreement on several points, there is the widest divergence on others, the causes for which are partly apparent from the reported outlines of analysis, which in the case of analyst 11 is open to serious criticism.

SUMMARY.

To summarize briefly, the most striking defects revealed are inability (1) to determine alumina correctly or even to get a fairly correct collective weight for the substances that are precipitated by ammonia; (2) to determine small amounts of manganese gravimetrically with any approach to accuracy; (3) to make an acceptable alkali determination, especially as to soda; (4) to determine the so-called combined water with any approach to accuracy. Similar comment might be made regarding the carbon of carbonaceous matter, but the determinations are altogether too few to justify sweeping condemnation. In individual cases certain errors are manifestly due less to lack of skill in manipulation than to ignorance of the normal composition of a limestone as to the minor ingredients and their manner of combination, or to failure to ascertain the qualitative composition of the material beforehand and thus avoid pitfalls. This last defect is naturally rather more evident in the students' work than in that of instructors, and yet it is to be supposed that the former were super-

[1] These values were reported as "Al_2O_3," but probably cover most if not all of the TiO_2.

[2] Localization of alkalies in the insoluble assumed by analyst from other evidence than actual test and doubtless justified.

vised by their instructors, who are therefore responsible for lapses of the kind named. Two or three instances may be given. One student found but 0.03 per cent. of water escaping between 105° and 250°, and, apparently ignorant of the fact that silicates often retain much at even higher temperatures, was led to ascribe far too high a value to carbonaceous matter, which he derived from "ignition loss" by deducting CO_2 and H_2O. Another student determined FeO by solution in sulphuric acid and titration with permanganate, unmindful of the effect of carbonaceous matter and possible soluble sulphide of iron. Still again, one determined CO_2 by loss in weight of his apparatus after using nitric acid to decompose the carbonates, ignorant perhaps of the presence of iron sulphide and ferrous carbonate and of the effect of these as well as of carbonaceous matter upon that acid.

Although the students' analyses are not all by those who were about to close their undergraduate studies, it is very evident that few if any of those who made them are fitted as yet to offer their services to the public as analysts.

In spite of the relatively small number of analyses from instructors and students, it is probable that the returns are in general indicative of the situation as to analytical chemistry throughout the country. Good work is apparent in several instances, but a great lack of it in far too many, and the charge referred to in the opening sentences of this report seems to be measurably sustained. It is evident that much greater attention should be paid to the training in analytical chemistry of those who are to fit future generations of chemists to do competent work in analysis. In order that they may accomplish this it is plain that they should be given greater opportunity to perfect themselves practically. Knowledge of the theory of analytical operations and separations is not sufficient. Among the points needing greater attention are control of reagents, impressing the importance of this upon students, and greater opportunity for them to verify the correctness of their work. Only by such means will it be possible to raise the standard of analytical chemistry above the low plane it now occupies in so many fields.

In this connection, passages in two letters of very recent date that passed between a professor of analytical chemistry in one of our eastern colleges and the chairman of the subcommittee on zinc-ore analysis, Mr. Geo. C. Stone, may be most fittingly quoted.

The first writer, freely admitting a most disgraceful state of the analytical art as evinced by the published analyses of selected samples of zinc-ore,[1] demurred to the suggestion that this might be mainly due to our poor methods of teaching. "As you well know, our students come to us from every walk of life. Some have had the advantage of a very superior secondary education, but the great majority come to us with their faculties untrained, with no sound habits of study and with no ambition for anything higher than an analytical position in some steel works laboratory. This great majority are not possessed of a critical mind or a spirit of investigation. They will perform an analytical operation a dozen times and learn nothing more than to follow directions, and in many instances they are unable to properly interpret directions, owing to their lack of a good general education. Without doubt the teaching is at fault, but it seems to me that the improvement must begin at home and continue through the primary, intermediate, grammar and high school grades before we can expect better results from our college graduates."

To this Mr. Stone replied in part: "....I fully agree with you that the improvement should begin with the lower grades. Where I do think that the colleges and universities are greatly at fault is in being so easy in their requirements that students who are not properly prepared are allowed to enter and graduate. I also think that any system of teaching analytical chemistry that allows the student to 'perform an analytical operation a dozen times and learn nothing more than to follow directions,' is wrong and will produce the sort of results that we received for samples 'A,' 'B' and 'C.'.....It seems to me that the functions of our institutions for higher education should be, *1st*, to eliminate those who from lack of brains or preparation are not capable of profiting by the education, and, *2nd*, to give those who are worthy of it a thorough training."[2]

These views supplement in the clearest manner some of those

[1] This Journal, **26**, 1648–1649.

[2] Certain references in this last quotation receive singular justification by the remarks accompanying the analysis furnished by one instructor. From these it might be inferred that it is not the principles of analysis which are understood and taught in the institution, but simply rule of thumb methods applicable to the particular products of a certain section of country.—Note added by the chairman.

expressed by the chairman of this committee in his address at Philadelphia a year ago.[1]

The committee does not feel called upon to make specific recommendations based upon the showing of the above table of analyses. It prefers for the present to let the table and the above-quoted remarks speak for themselves to each and every instructor. It believes that their consideration ought to lead to much good, and that the seed of improvement already germinating will in time produce good fruit if continuously and carefully cultivated.

W. F. HILLEBRAND, *Chairman.*
CHAS. B. DUDLEY,
CLIFFORD RICHARDSON,
H. N. STOKES.

REVIEW.

SOME ABSTRACTS FROM CURRENT LITERATURE UPON INDUSTRIAL CHEMISTRY.

BY FRANK H. THORP.

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This article being a continuation of the Review prepared by the writer last year, the same general scheme has been followed. As in the previous article, attention has been given mainly to papers published in the foreign journals during the year just closed, and which have not been included in the *Review of American Chemical Research*. A few abstracts from American journals and patents have been given. It has been desired to make the abstracts brief and to consider only those which seemed of most general interest.

Technical Education.—Technical training and educational methods continue to receive attention in society meetings and technical journals. Prof. Sir Alexander Kennedy, in an address before the Union Society of University College, London, referred to the Academic Side of Technical Training. He argued that the teaching of various branches should be carried much further than the point which may just suffice for the needs of the professional work of the engineer. A scientific branch cannot be mastered, even to an elementary degree, without some knowledge of the more advanced phases of the subject. He holds it essential that advanced work shall be done, but this should be so selected that it will make clear and certain the knowledge of the early work. It is necessary to broaden the mental grasp of a

[1] This Journal, 27, 300.

subject so that the individual may be able to think beyond the limits of daily routine work. In this country, a paper by Prof. H. M. Howe before the Association of American Universities, dealing with the question of association of technical schools with large universities, has attracted much attention. The author inclines to the view that "wisely guided association" is beneficial to both the technical school and the community.

Acids.—Berl (*Z. angew. Chem.* **18,** 252 (1905)) has experimented with arsenic pentoxide as a catalyzer for the preparation of sulphur trioxide. He finds that arsenic pentoxide acts catalytically about as do ferric oxide and vanadium pentoxide, thus supporting the views of Lunge and Reinhardt (this Journal, **27,** 417). Sulphuric acid appears to be the best means of drying the gases, since better results were obtained with gases so dried than when more thoroughly dried or if more moisture were present. The speed of the reaction increases with greater concentration of either the sulphur dioxide or the oxygen, but more noticeably in the case of the sulphur dioxide. Any sulphur trioxide remaining in the apparatus diminishes the speed of the reaction and is supposed to crust over the surface of the contact material and hinder the diffusion of the gases. Owing to its greater density and slow diffusion, carbon dioxide is found to retard the reaction more than does nitrogen, thus supporting the view that the process is a diffusion reaction. It is also asserted that sulphur trioxide at high temperatures, 300° to 500° C., corrodes glass. Küster and Münch (*Z. anorg. Chem.* **43,** 350 (1905)) tried to make 100 per cent. nitric acid by crystallization in perfectly dry air, but the highest concentration they could get was 99.4 per cent. By excluding the air they succeeded in raising the concentration to 99.79 per cent. On standing in dry air, the acid lost strength until a concentration of 98.67 per cent. of HNO_3 was reached. The authors conclude that absolute nitric acid only exists as crystals and at temperatures below —41° C. The crystals decompose when melted and the resulting nitrogen pentoxide and water dissolve in the acid. This is supported by the observation that the crystallized acid of melting-point —41.3° was pure white, but the melted acid at even —41° C. had a yellow tinge. On passing perfectly dry air through the yellow liquid, the nitrogen pentoxide was driven off and a colorless acid of 98.67 per cent. strength remained. This could be distilled unchanged. Lüty (*Z. angew. Chem.* **18,** 1253 (1905)) reviews the present progress and economies in the chamber process for sulphuric acid. A short abstract of the paper can only be unsatisfactory, owing to the number of details discussed. The yield of acid has been increased, by means of improvements in the process, to 6 or 7 kilos chamber acid per cubic meter chamber capacity per day. About 12 to 14 cubic feet of chamber space per pound of sulphur burned per day is now customary. Raschig

(*Ibid.* p. 1281) has another long paper on the theory of the chamber process. The reactions taking place in each part of the system are discussed separately and the causes of loss in several instances are pointed out. Lunge (*Z. angew. Chem.* **18,** 60 (1905)) disputes certain contentions of Raschig (this Journal, **27,** 417) that nitrosylsulphuric acid causes the nitrous character of chamber acid, and that the small percentage of nitrogen trioxide in chamber acid is equivalent to only 0.1 per cent. nitrosylsulphuric acid. But this amounts to 2,000 kilos in a production of 2,000 tons of acid. The author found in the chamber acid and "drips acid" in a works in Zurich, 0.085 and 0.24 per cent. of nitrosylsulphuric acid. The fact that nitric oxide yields nitric acid and nitrous acid, when shaken with air and water, is claimed to have no bearing on the chamber process, since there is almost no nitric acid formed. But in Raschig's experiments, having a great excess of water vapor, he changed the entire nature of the reaction and converted nearly all the nitric oxide into nitric acid. Haber and Oordt (*Z. anorg. Chem.* **43,** 111 (1905)) have produced ammonia directly from nitrogen and hydrogen, by passing the mixed gases over powdered iron, supported on asbestos and heated to above 1000° C., in a tube. A few experiments were made with nickel powder produced by reducing the nitrate with hydrogen. This was less effective than the iron. The mixture of gases was prepared by decomposing ammonia in a similar apparatus by passing it over the iron at 1000° C.; the undecomposed ammonia was absorbed in standard acid and the purified gases again conducted over the heated iron to reform ammonia. An equilibrium was soon reached in both cases. Lunge and Berl (*Chem. Ztg.* **28,** 1243 (1904)) have studied the reaction between nitric oxide and oxygen or air, by passing measured amounts of the gases into a flask with varying quantities of water. After definite times, concentrated sulphuric acid was added to absorb the nitrous gases. The total nitrogen was then determined in measured portions of the acid by means of the nitrometer and the nitroso compound by use of permanganate. It was found that (1) the amount of water was the chief factor in influencing the formation of nitric acid from the nitric oxide. The conversion was complete with a certain proportion, but excess of water beyond this point resulted in a larger yield of nitrous acid. (2) The presence of free nitrogen with the oxygen (as in air) had no effect on the formation of nitric acid, the amount of water being the important factor. (3) The reaction is not instantaneous but requires some time. (4) Concentrated sulphuric acid is better than alkali hydroxides for absorbing nitrogen oxides, since it forms stable compounds, while the latter form bodies capable of further reaction, and thus affect the value for total nitrogen. Carpenter and Linder have continued their study of the reactions in the Claus kiln (*J. Chem. Ind.* **24,** 63

(1905). Compare this Journal **27,** 415 (1905)). They give their observations of the influence of various contact substances on the interaction of steam and hydrocyanic acid (for the formation of ammonia), both in the presence of hydrogen sulphide and air, and in their absence. The apparatus is first described, with an account of the methods of analysis and of calculation. Experiments were carried on using broken brick, oxide of iron and Weldon mud, in the absence of hydrogen sulphide and air. It was found that the reactions, (1) $HCN + H_2O = NH_3 + CO$ and (2) $CO + H_2O = CO_2 + H_2$, occur simultaneously but with lower temperature than 530°, as had been stated (*J. Gas Light.* (1902) p. 1417) *viz.*, between 465° and 625°, about 80 per cent. of the hydrocyanic acid is converted to ammonia, but some of the acid escapes undecomposed, the amount increasing with increased rate of flow. Carbon monoxide and hydrogen are constant products of the reaction, the hydrogen being in excess. No pronounced decomposition to free nitrogen was observed, even at 625°. With oxide of iron, under the same conditions, the yield of ammonia reaches a maximum (96.5 per cent.) at about 280°, and then falls rapidly. No undecomposed acid was found. Below 350° hydrogen and carbon monoxide were formed; at higher temperatures (500°), these were oxidized by interaction with the contact material. Below 350° the oxidation of the ammonia or the hydrocyanic acid was not marked, but above 500° it was very pronounced. These experiments show that the reactions (1) and (2) above both occur within the temperature range 200° to 350°; at 500° the only products were nitrogen, carbon dioxide and ammonia. With Weldon mud the yield of ammonia never exceeds 75 per cent.; hydrocyanic acid escapes undecomposed under 150° C. and above 200° C. free nitrogen appears in the products. These results show Weldon mud to exercise a much more powerful oxidizing action upon the reaction products than does iron oxide, since no carbon monoxide nor hydrogen are found in the products. In the presence of hydrogen sulphide and air, with the same apparatus and contact substances, a similar series of tests was carried on. The proportion of air was in moderate excess of that needed for the decomposition of sulphur and water. This introduction of air vitiated, to a great extent, the importance of the figures for nitrogen. With brick contact, the hydrogen sulphide and air favored a high yield of ammonia, but did not sensibly affect the character of the products. The most favorable proportion of air for maximum yield is 3.2 air to 1 hydrogen sulphide. Nitrogen and undecomposed hydrocyanic acid were absent from the product, but both carbon monoxide and hydrogen were found when the air did not exceed the above proportion. With higher proportion of air, only free nitrogen, ammonia and carbon disulphide were in the product. With oxide of iron it was again found that air and hydrogen sulphide

favored a high yield of ammonia, and there was absence of undecomposed hydrocyanic acid, carbon monoxide and hydrogen. With Weldon mud, the presence of air and hydrogen sulphide again favored high yield of ammonia and also modified the nature of the products. For maximum yield of ammonia, the best proportion of air to hydrogen sulphide was found to be 2.7: $1H_2S$, with a temperature of 380°. Carbon monoxide and hydrogen were present and nitrogen absent between the temperatures 220° to 380°. As to the distribution of ammonia, it is present in the exit flue gases of the kilns as ammonium sulphate mainly, but to a less extent as ammonium sulphite, or more probably thiosulphate. Special attention was given to the estimation of the various oxidized sulphur compounds of ammonia in the residual gases, resulting from the interaction of steam and hydrocyanic acid in the presence of hydrogen sulphide under the conditions existing in the Claus kiln. By filtering the gases through asbestos at 100° to 200° C., before passing them to the acid catch for ammonia absorption, the large dilution and decomposition by secondary reaction with the half-normal acid was avoided. The asbestos was then extracted with cold water and the extract examined. With Weldon mud (sulphided) and the temperature not above 380°, the results showed the presence of traces of oxidized sulphur compounds in the asbestos and the absence of sulphate, most of the ammonia appearing as carbonate. With oxide of iron (sulphided), at temperatures of 480° to 520°, one experiment showed the presence of oxidized sulphur compounds of ammonia in the asbestos and an absence of sulphate in the acid catch. With broken brick at 565° to 580°, there was absence of pentathionate, sulphate and thiosulphate in both the asbestos and acid catch, and a large proportion of ammonium carbonate. Tabulated results of the experiments, and curves of the most important features of the tables, are included in the paper. Eyde and Birkland's process for nitric acid from air by electric discharges (*French Pat.* No. 335,692, 1903) is described in *Z. Elektrochem.* 1905. Winteler (*Chem. Ztg.* **29,** 820 (1905)) discusses nitric acid making to meet the modern demands for explosives, and the production of nitrated cellulose for celluloid and artificial silk. Freedom from nitrous acid is desired for these purposes. Analyses of two American-made mixed acids for nitrating, are given. The best conditions for manufacturing are (1) keeping the temperature as low as possible in the retort and carrying on the process very slowly to avoid overheating. (2) The niter should be dry, and the best strength for the sulphuric acid is 92 per cent. (3) The yield is better if air be introduced into the retort. (4) Rapid condensation of the vapors is essential. The utilization of the acid sulphate for hydrochloric acid making is considered, and also the effects of impurities, such as nitrate, nitrite, sulphuric acid, chlorides, iodine compounds, arsenic and selenium.

The latter passes into the hydrochloric acid and colors it red or yellow and causes it to dissolve copper. Guttmann (*Loc. cit.* p. 934) comments on the above paper and replies to certain criticisms of Winteler upon data given by himself. Saposchnikow (*Z. physik. Chem.* **51,** 609 (1905)) has examined mixtures of concentrated nitric (sp. gr. 1.467) and concentrated sulphuric acids, with respect to the vapor-pressures. The percentages used ranged from 100 of nitric acid and no sulphuric, to 5.29 per cent. nitric and 94.71 per cent. sulphuric acid; in all, 12 mixtures were examined. The vapor-pressure (in millimeters of Hg) ranged from 16.64 for 100 per cent. nitric acid to 34.12 mm. for a mixture of 59.91 nitric to 40.09 of sulphuric acid. The pressure then decreased to 8.40 mm. for a mixture of 20.07 per cent. nitric to 79.93 sulphuric acid. The highest vapor-pressure is found with a mixture of 65 per cent. nitric acid (sp. gr. 1.48) and 35 per cent. sulphuric acid, corresponding to $5HNO_3+2H_2SO_4+3H_2O$. In a later paper (*Loc. cit.* **53,** 225) the author continues his work with nitric acid (sp. gr. 1.40) containing 65.3 per cent. nitric acid and pure 100 per cent. sulphuric acid. The results show similar effects by the addition of the sulphuric acid; the mixture of acids is less active in nitration work but still admits of highly nitrated products being prepared. Bodenstein and Pohl (*Z. Elektrochem.* **11,** 373 (1905)) have studied the contact process for sulphuric acid, with reference to the law of mass action, to ascertain if the formula,

$$\frac{C^2_{SO_2}\, C_{O_2}}{C^2_{SO_3}} = K,$$

(a constant) applies where C is the concentration. A steady current of sulphur dioxide and air was passed over a platinum contact mass in a quartz tube, heated uniformly in an electric furnace, and the composition of the resulting gas mixture compared with that entering the tube. Fourteen experiments were carried on at about 727° (=1,000° abs.), and the results corrected to equalize the variations of temperature, pressure, rate of passage through the apparatus, and quantity of sulphur dioxide per volume of oxygen. The sulphur trioxide produced ranged from 20.8 to 59.6 per cent. of the amount of sulphur dioxide originally present. The value of K was found to vary from 3.43×10^{-3} to 3.67×10^{-3} and averaged 3.54×10^{-3}. The results of other experiments at different temperatures agreed with these, and it was further found that the heat evolved in the reaction $2SO_2+O_2=2SO_3$, as calculated from these results, agreed with the observed values. The authors hold that the reaction obeys the law of mass action closely. Lunge (*Chem. Ztg.* **29,** 933 (1905)) defends the work of Rey and himself in determining the specific gravity and strength of nitric acid (*Z. angew. Chem.* (1891) p. 165) against the criticism by Winteler, and shows that curves of their results plotted along with those from the work of Kolb,

Veley and Manley, and of Ferguson agree reasonably well and throw doubt on the correctness of Winteler's figures. Winteler (*Chem. Ztg.* **29,** 689 (1905)), finding that the specific gravity tables for nitric acid of high concentration were inaccurate owing to the presence of nitrous acid, has made redeterminations of the gravity and concentration on especially purified acid of various strengths, ranging from 47.0° to 49.4° Bé., corresponding to percentages of HNO_3, 86.3 to 99.7 respectively. Ferguson (*J. Chem. Ind.* **24,** 781 (1905)) describes the method employed by himself and his assistants in preparing the tables of specific gravity of sulphuric acid, nitric acid, hydrochloric acid and ammonia, which have been adopted by the Manufacturing Chemists' Association of the U. S. The tables also are published in full. Nagel (*Electrochem. Metal. Ind.* **3,** 16 (1905)) suggests the conversion of electrolytic chlorine into hydrochloric acid by passing it with steam through incandescent coke at 1000° C., thus: $Cl_2+2H_2O+2C=CO_2+CO+2H_2+2HCl$. This he asserts would be more profitable than the manufacture of bleaching-powder. The gases are passed through absorbing towers and the unabsorbed mixture of carbon monoxide and hydrogen may be utilized for fuel purposes. Deussen (*Z. anorg. Chem.* **44,** 300 (1905)) has determined the conductivity and strength of solutions of hydrofluoric acid, and its influence on the rate of inversion of cane-sugar. In this latter case, it appears to come between monobasic and dibasic acids. It is a little weaker than phosphoric acid of equal concentration. Dubosc (*Rev. Gén. Mat. Col.* **9,** 99 (1905)) proposes to make hydrosulphites by heating the acetone-sodium bisulphite compound with ammonium formate solution. A sesquicarbonate of ammonia distils off and the solution of hydrosulphite is evaporated *in vacuo*. Ammonium formate is preferred as it is volatile at 60°, and the reaction with the sodium bisulphite compound goes on at 84°. Lead, zinc or manganese formate can, however, be used instead. Tarugi (*Chem. Centr.* **1,** 584 (1905)) has found that bleaching-powder or hypochlorite which becomes pink on exposure to carbon dioxide, contains iron, probably in the form of calcium ferrate. Manganese does not appear to be present, contrary to the generally accepted view as to the cause of the color. Wegschneider and Walter (*Monatsh.* **26,** 685 (1905)) have prepared a table of densities and percentages at 60° C., and 80° C., for sodium carbonate and sodium hydroxide. Interpolation formulae for calculating densities of these solutions at all temperatures between 0° and 100° C., for concentrations up to 8 N, are given.

Salts.—Winteler (*Electrochem. Metal. Ind.* **3,** 16 (1905)) has examined samples of electrolytic caustic potash for strength and finds the content to vary from 73.3 to 81.8 per cent. of potassium hydroxide, while the carbonate ranges from 2.4 to 18.4 per cent. As no carbonate is formed in electrolysis, this im-

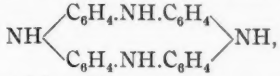
purity comes from contamination during the evaporation and casting of the caustic. By shaking hot solutions of 1.5 sp. gr. with solid potassium carbonate, and then cooling down to 20° C., the amount of carbonate remaining in the solutions ranged from 37 to 55 grams per liter, while the hydroxide amounted to 700 to 760 grams per liter. This is considered the limit which may be produced by absorption of carbon dioxide, hence any quantity in excess of this found in solid caustic has been formed in the casting operation. Fused hydroxide, on standing, deposits most of its content of carbonate, and the clear portion should not contain over 3 to 5 per cent. of carbonate. Geffekin (*Z. anorg. Chem.* **93,** 197 (1905)) has determined the solubility of lithium carbonate in various alkali salt solutions, and prepared curves of the solubilities. It appears that alkali sulphates, especially ammonium sulphate, have very considerable solvent power on lithium carbonate. Frasch (*J. Chem. Ind.* (1905) p. 17) describes his method for making caustic soda (U. S. Patent, 688,463, 697,465) in which ammoniacal salt brine is treated with nickel hydroxide, forming nickel-ammonium chloride ($Ni(NH_3)_2Cl_2.4NH_3$), and caustic soda. The nickel-ammonium chloride is insoluble in the caustic liquor, and is filtered off and distilled to recover the ammonia and the nickel hydroxide, both being returned to the process. The amount of nickel hydroxide is about 8● per cent. of the salt converted, but is affected by the amount of water in the hydroxide. If the hydroxide recovered in the process contains 60 per cent. of nickel hydroxide, 200 grams per liter of ammoniacal brine yield 10 per cent. caustic soda solution, and 73 per cent. of the salt in the brine is converted. The reaction takes about an hour. The nickel-ammonium chloride is easily decomposed by water to nickel hydroxide and ammonium chloride, so for high conversion and strong caustic liquor any excess of water is avoided, and rather an excess of salt is used to keep the brine saturated as the ammonia is abstracted. The salt also serves as filtering material to separate nickel-ammonium chloride from the caustic liquor, this being done in the same vessel as the conversion. The nickel oxide and ammonia are recovered by distillation in a calcium chloride solution of 1.250 sp. gr., which is saturated with salt. The nickel-ammonium chloride is suspended in the calcium chloride solution in the proportion of 400–500 grams to the liter, and distilled. The ammonia in excess of that in the form of chloride is driven off, and the nickel hydroxide is precipitated and removed by decanting or filtering. If the calcium chloride is allowed to concentrate to its practical limit before drawing off, not over 600 gallons of waste liquor are produced per ton of caustic soda. The time required for distilling the ammonia and separating the nickel is four hours to a charge of 10,000 gallons, which produces about four tons of caustic soda. If the conversion and

distillation be conducted in the same apparatus to prevent loss of nickel and ammonia, an additional four hours is needed for conversion, filtration and washing; or, about 10 tons of caustic soda per day is the output. Hempel (*Z. angew. Chem.* **18,** 132 (1905)) has studied the production of phosphorus by the Pelletier process, in which tricalcium phosphate is converted to the monocalcium phosphate with sulphuric acid and this is then reduced with charcoal. An excess of sulphuric acid over the calculated amount is needed to render the phosphate soluble, and when the liquors are evaporated to a specific gravity of 1.28, the sulphuric acid is 4.2 per cent. At this point the crystallization of the phosphates begins, so the concentration is stopped. It proved difficult to make an apparatus for the reduction of the phosphorus; the vapors passed through the walls of fire-clay retorts, and porcelain vessels became clogged. Collection of the phosphorus by scrubbing with liquid was not entirely successful, but filtration through a layer of garnet sand worked well. The reduction was accomplished in a porcelain tube wound with a coil of nickel wire through which a current was passed for heating. This tube was jacketed with another of fire-clay which in turn was surrounded by diatomaceous earth. Temperatures were taken with a thermo-electric pyrometer inserted into the tube. A wide delivery pipe conducted the vapors to a washing vessel from which they passed to the garnet filter, and then to a final wash-bottle. Lastly, the gases passed through a meter before escaping into the air. Between 300° and 600°, the sulphuric acid present is reduced and passes off as sulphur dioxide. At 700°, the gas contains carbon dioxide, carbon monoxide and hydrogen and becomes combustible. At 74° distillation of phosphorus begins, being most active above 960°; at 1170° practically all the phosphorus was over. About 92.5 per cent. of the phosphorus was recovered in the condenser, but some of it refused to melt together (probably due to a little hydrogen phosphide as solid or liquid) and had to be determined by oxidation and weighing as pyrophosphate. Metaphosphoric acid did not afford a good yield of phosphorus, as it did not reduce with the charcoal. The old reaction $Ca_3P_2O_8 + 3SiO_2 + 5C = 3CaSiO_3 + 5CO + 2P$, proposed by Wöhler, which could not be carried on technically because of the high temperature necessary, becomes possible here. The reaction begins at 700°, and phosphorus is evolved at 1150°, but only between 1200° and 1450° is the evolution brisk; above 1450° the process ceases. A yield of 92 per cent. was obtained, which was not improved by higher heating. In Germany the process is worked in electrically heated sheet-iron cylinders lined with fire-clay. The slag is run off continually. For high yield, the materials must be perfectly dry. Bauer (*Chem. Ztg.* **29,** 1 (1905)) describes a method for making lead acetate on a large scale. To avoid loss in evaporation, acetic acid of 60 per cent.

concentration is used. Pure litharge, free from iron and alumina, is added in 100 kg. portions to the total quantity of acid in a vat provided with a reflux condenser and a wooden stirrer. In about an hour the litharge is dissolved, the temperature not being allowed to exceed 65°. The liquor should then stand at 70° to 72° Bé. at 65°. It is settled in covered vats in which sufficient mother-liquor from previous crystallizations has been mixed with the fresh liquor to bring the gravity down to 50° Bé. By hanging metallic lead plates in these vats, any copper is precipitated; after standing about six hours, at a temperature slightly above 60°, the solution is filter-pressed and goes to the crystallizing vats where it stands a week or ten days. The vats are covered and provided with steam coils, so the cooling can be controlled, and about 3° per twenty-four hours is the rate of cooling desired. The crystals are freed from mother-liquor in centrifugal machines and dried in vacuum driers at 30°. The mother-liquors have a density of about 35° Bé. and are returned to the vats with the next liquors. All residues are extracted with water and the wash-waters evaporated. Lumière and Seyewetz (*Rev. Gén. Mat. Col.* **9,** 250 (1905)) show that sodium hydrosulphite may be kept unoxidized indefinitely in dry air, but in moist air oxidation proceeds rapidly. In distilled water which has been boiled, the salt is oxidized slowly if the solution be dilute (3 per cent. solutions in sixteen days and more rapidly as the concentration is higher, a 10 per cent. solution in eleven days and a 25 per cent. solution in three days). In the presence of air, the oxidation is greatly accelerated. Certain substances appear to retard the oxidation; *viz.*, trisodium phosphate, acetaldehyde, benzaldehyde and trioxymethylene in connection with sodium sulphite; the first has no deleterious effect on the indigo-reducing power in cold solutions; the others retard reduction until the temperature is near 100°. Naumann (*Ber.* **37,** 4328, 4609 (1904)) has determined the solubility and certain reactions of a large number of inorganic salts in acetone and pyridine. The work is a continuation of an investigation published in 1903 (see *J. Chem. Ind.* (1904) p. 1088). Frank and Voigt have patented processes for cyanide and ammonia from cyanamide (*U. S. Patents*, Nos. 775,953 and 776,314). For cyanide, a metallic cyanamide is fused under pressure with flux, carbonaceous matter and a base whose cyanide is to be formed. For ammonia the cyanamide is heated under pressure with carbon dioxide gas and water in proportions of at least three molecules to each two atoms of nitrogen in the cyanamide, the temperature being at least 100°. At about 300°, under the above conditions, ammonia and a formate are produced.

Dyes.—Barbier (*Bull. Soc. Indust. Mulhouse* (1905), p. 153) describes a new group of direct (azo) dyes obtained from diphenyl in combination with tetrazo-derivatives from benzidine, toluidine,

dianisidine, *p,p'*-diaminophenyltolyl and similar diamines. The colors yielded by these products range from red through orange, yellow, blue to violet. They are direct cotton dyes, fast to acids. Prud'homme (*Ibid.* p. 155) describes new hydrazine sulphonate dyestuffs obtained from basic dyes, such as magenta, safranine *p*-nitraniline, etc. These are acid dyes, coloring wool in acid baths. Shades of prune, red, green, blue and yellow are obtained. Vidal (*Monit. Scient.* **19,** 25 (1905)) discusses the presence and action of mercaptan groups in the direct sulphide dyestuffs. He holds that the solubility of these dyes in alkali sulphide solutions is not due to the presence of the mercaptan groups, but that they appear to modify the shades of the color in some cases, but are not necessary to the formation of the dye. Certain reactions are proposed to represent the formation of sulphide dyes from *p*-aminophenol. The same author (*Z. Farben. Textil. Ind.* **4,** 458 (1905)), by heating quinol with *p*-phenylenediamine to 180° C., in sealed tubes, produced a leuco-base of emeraldine and azuline, which, on further oxidation of the dyes, yielded aniline black. Goppelsroeder's formula for aniline black,



seems to be supported by this.

Bleaching.—Störmer (*Centr. Bl. Bakter. Parasitenk.* **13,** 35, 171, 306 (1904); *Chem. Centr.* **1,** 41 (1905)) has studied the retting of flax under water. The process is a fermentation induced by organisms, mainly of the anaerobic *Plectridium* genus, which attack the pectin bodies of the material enclosing the fibres. Absence of oxygen is essential for the process, and this is secured by the action of certain oxygen-consuming bacteria; hydrogen, carbon dioxide and organic acids, such as acetic, butyric, and lactic, are then produced. Since butyric acid is injurious, it is proposed to add lime to the liquid during the retting and to use pure cultures of *Plectridium.* Knecht (*J. Soc. Dyers Colorists,* **21,** 189 (1905)) has found that human saliva has action on bleached cotton, whereby the fibre is made to take up more dyestuff. Probably the ptyaline is the active agent. It is suggested that this action may account for some of the spots on piece goods which occasionally appear in the finished product. Trotman (*J. Chem. Ind.* **24,** 267 (1905)) discusses the damage caused by magnesium soaps in bleaching. He classifies the brown discolorations on bleached goods as due (1) to iron, (2) overbleaching, (3) mildew, (4) grease, (5) use of unsuitable soaps and water. The last is held to be of very common occurrence, while overbleaching is not very frequent. Damage, showing after a considerable length of time, particularly in a hot climate, has frequently proved to be due to resinate of lime or

magnesia. Waters used in bleaching often carry lime and magnesia and are used without purifying, while many soaps contain considerable resin. The lime and magnesia resinates are insoluble in water and when dried, slowly become brown, partly because of dehydration. Magnesia soap is distinctly darker than the lime soap.

Dyeing.—Hurst (*J. Soc. Dyers Colorists*, **21,** 130 (1905)) has studied the mordanting of silk with regard to the diminution of lustre if the temperature is high. The mordant oxides appear to deposit on the surface of the fibre as minute excrescences at about 140° to 150° F. and at higher temperatures the oxides penetrate further into the fibre and dull the lustre. Between 70° and 120° F., there was no loss of lustre by the mordanting, but the process is very slow. Above 150° F., only chromium bisulphite could be used safely and this gave good results when heated to 180–190° F., the loss of lustre being very slight. Green, Yeoman and Jones (*Ibid.* **21,** 236 (1905)) have prepared quantitative analytical tables for detecting dyestuffs in animal fibres. The scheme is based principally on the stripping effect of various reagents, combined with reduction tests with sodium hydrosulphite and reoxidation tests with a persulphate. Seven tables for the various colors are given. Suida (*Monatsh.* **26,** 413 (1905)) has examined the relation between the chemical composition and the dyeing properties of cotton, wool and silk. Regarding cellulose as an alcohol body containing hydroxyl groups, its chemical activity is attributed to these groups probably having a slightly acid nature. Purified cotton was heated with acetyl and benzoyl chlorides, dimethyl sulphate and caustic soda, and alcohol and sulphuric acid. The two chlorides were found to introduce one acyl radical into each cellulose molecule. The reaction products were washed and dyed with samples of the original cotton and of nitrated cotton (12.1 per cent. nitrogen) in magenta and crystal violet (basic dyes), Bordeaux extra (a direct dye) and azofuchsine B (acid dye). The cellulose and its acyl and alkyl derivatives took the basic and direct dyes readily and to an equal degree, but the acid dye was not absorbed. This showed that the introduction of these groups into the cellulose molecule had not affected the activity of the hydroxyl groups, which is evidently very slight in any case. Purified wool was treated with acetyl chloride, acetic anhydride, ethyl bromide and alcohol and sulphuric acid. The samples were washed with alcohol and water and dyed, together with the original wool at 80° to 90°, with the same basic and acid dyes as before. Only a slight tint appeared in the alkylated and acetylated samples with the basic dyes, but the original wool took the color deeply; but with the acid dye these conditions were reversed, the treated wool taking the color well. Wool, boiled in weak sulphuric acid and washed, takes acid and basic dyes about equally well. The

treated wool, when heated with ammonium carbonate, regained its original properties, thus showing that an anhydride is not produced by the reagents. These appear to act on the carboxyl group in the first instance and then on the amino-group, in the latter case producing a salt. Silk is not affected as to its dyeing properties by these reagents except the alcoholic sulphuric acid, which alters its character on heating. Such treated silk takes acid dyes well from a neutral bath, but is merely stained by basic dyes. Wool and silk dyeing with these dyestuffs thus appears to be a simple chemical action. Sedlaczek (*Färber-Ztg.* **16,** 17 (1905)) describes a method for dyeing leather with sulphide dyes, in which tannin or glucose is added to the dye-bath to prevent injury to the leather by the sodium sulphide. The author also reviews the methods of producing yellow and brown shades on tanned leather by soaking in solutions of titanium salts; these salts also serve as mordants for certain dyewoods. Alcoholic or aqueous solutions of *p*-phenylenediamine, *p*-aminophenol or *p*-diaminodiphenylamine are said to be satisfactory hair dyes. By oxidation through exposure to air or by hydrogen peroxide, various shades of brown are obtained. Kapff (*Färber-Ztg.* **15,** 357 (1904)) discusses the use of formic acid in dyeing and printing. By adding it to the bath for wool dyeing, uneven deposition of color, such as occurs with sulphuric or acetic acid, is largely avoided and the fibre takes up a larger amount of dye. In dyeing mixed silk and wool, formic acid is recommended in place of acetic or oxalic acids, as it causes fuller shades on the silk. It is most largely used with potassium bichromate for mordanting wool; 1.5 per cent. of formic acid (85 per cent.) liberates the chromic acid of the bichrome and entirely reduces it, fixing the chromic oxide on the fibre after about two and a half hours boiling. The acid also counteracts any lime in the water used for dyeing. It is also proposed for use with bichrome for "after-chroming" dyed goods. For printing methylene blue, magenta and auramine, lighter and more brilliant shades are obtained than with acetic acid. Five per cent. of the acid will keep a starch paste in good condition much longer than when no acid is present. It may also be used to impart a "scroop" feel to mercerized cotton, and is better for this than acetic or sulphuric acid and less expensive than citric or tartaric acids. Mettner (*Z. Farb. Textil-Chem.* **4,** 171 (1905)) contributes an article upon the use of formic acid in wool-dyeing. With this assistant, there is more complete absorption of the chromium by the wool fibre, and it is claimed that the dyeing can be carried out in the same bath in which the mordanting has been done. Such dyeings are reported to be very fast to milling and better than when mordanted and dyed in separate baths. The wool is mordanted with 1.5 per cent. of its weight of potassium bichromate, with 2 per cent. of formic acid (80 per cent. strength),

and heated to gentle boiling for an hour and a half to two hours. Cold water is then added to the bath to reduce the temperature, and the color solution added in small portions; finally about 2 per cent. of formic acid is added and the dyeing completed by boiling for two hours. Dreaper (*J. Chem. Ind.* (1905) p. 233) publishes a contribution to the theory of dyeing, basing his conclusions largely upon experiments made with colloidal solutions of arsenious sulphide. From the experimental results, he advances the following laws: (1) "Within certain limits of concentration, and when once an equilibrium has been established, and in the case of a solution where this action is a reversible one, the aggregates in any solution system are of equal size." (2) "The aggregates in a stronger pseudo-solution are larger in direct relation to the number of molecules present, and that, when once a certain point is reached, they increase in size rather than in number." The author rejects any chemical theory of dyeing and holds to the purely mechanical theory of the process. There is no evidence in favor of solid solution in any of his results. Lamb (*J. Chem. Ind.* **24,** 187 (1905)) confirms the analysis of sumac ash, communicated by Trotman (*Ibid.* **23,** 1137 (1904)). A sample of pure sumac was found to contain leaf substance, 72.5 per cent.; stems (mid-rib, etc.), 6.6 per cent.; stalks, 20.9 per cent. The ash determinations showed from leaf substance 6.3 per cent.; stems, 8.1 per cent.; stalks, 3.9 per cent.; average of whole sample, 5.89 per cent. Common adulterants of sumac, *Pistacia Lentiscus* and *Tamarix Africana* showed very high ash, *viz.*, 6.8 per cent. in the former and 10 per cent. in the latter. Knecht (*J. Soc. Dyers Colorists,* **21,** 3 (1905)) explains his method for determining certain dyestuffs when dyed on cotton fibre, by direct titration with titanous chloride. A piece of the fabric is boiled in hydrochloric acid (1:3) for five minutes to remove any chlorine; then carbon dioxide is passed into the solution, a measured amount of titanous chloride added, and the solution heated until the color is destroyed. Then it is cooled and the excess of titanous chloride is titrated with a ferric alum solution and potassium thiocyanate indicator. The carbon dioxide is passed in during the whole operation. The method gave good results with benzopurpurine 4B, chrysophenine, erika B, and brilliant yellow and methylene blue. With mixed colors a selective action appeared, the yellow being entirely destroyed before the blue was attacked. In the determination of methylene blue, the disappearance of the color gives a sharp end-point. Assuming that one molecule of dyestuff requires two atoms of hydrogen for reduction, accurate results are obtained by this method. Davidis (*Färber-Ztg.* **15,** 373 (1904)) proposes a new test for fastness of dyed cloth to perspiration, to replace the common test with acetic acid. Perspiration is usually of alkaline reaction and the test proposed is as follows: Prepare a solution

of 5 grams Marseilles soap and 3 cc. ammonia in one litre of water; steep the dyed fabric in this for ten minutes, then squeeze and wrap tightly around a glass rod with an interwound piece of cotton cloth. On drying at 50° the amount of "bleeding" of the color is taken as a measure of the fastness. The author recommends the use of formic acid instead of sulphuric for dyeing mixed goods with acid dyes, where the quantity of acid in the bath may tender the cotton. Lambrecht and Weil (*Ber.* **37,** 4326 (1904)) describes a colorless rosaniline hydrochloride, soluble in cold water with a very pale pink coloration. Williams (*J. Chem. Ind.* (1905) p. 877)) contributes a paper on the valuation of tannic acid from the standpoint of the dyer and calico printer. The author outlines the more important methods of tannin estimation, but considers Hunt's modification of the permanganate process (*Loc. cit.* (1885) p. 263) the most satisfactory. For rapid comparison of values, he uses a dye test on cloth printed with the tannins in question, and with a standard sample. The patches are then all dyed together in a bath of methylene blue, and the mordanting value and clearness of hue determined by comparison. Results nearer than 5 per cent. cannot be expected by the matching test, but it shows the colorist the relative value of the samples at a glance. Precipitation methods, using gelatin or hide powder, are not found satisfactory.

Cement.—Seger and Cramer (*Thonind. Ztg.* **28,** 1662 (1905)) have made tests upon bricks of Portland cement to which ground sand, iron, etc., had been added to increase their resistance to wear and crushing. Addition of ground ore increased the resistance to crushing somewhat, and also to attrition, but ground sand had a more marked effect and raised the figures considerably. The same authors (*Loc. cit.* p. 1687) have found that blast-furnace slag, used for Portland cements, varied a good deal, especially in the proportion of soluble silica and of alumina. A high percentage of sulphide was also found in the samples examined. There has been published a resumé of the standard requirements for Portland cement in Russia (*Chem. Ztg.* **28,** Rep. 391 (1904)).

Clays, Etc.—Heraeus (*Z. angew. Chem.* **18,** 49 (1905)) has determined the melting-points of various refractory clays, by heating in an iridium tube, 200 mm. long by 40 mm. diameter, heated by an electric current of 1200 amperes at 5 volts. The tube was jacketed in fused magnesia and cased in a fire-clay cylinder. A thermo-element of iridium and iridium-ruthenium calibrated to 1600° by a standard platinum-platinum-rhodium couple, and at 1780° in melting platinum, was used. (Recent determinations give the melting-point of platinum as 1710°.—Editor.) Calculations were made to give temperatures to 2000°. It appears that pure clays have a definite melting-point which is not changed by remelting the test piece. Determinations of the rate at which a weighted iridium rod settled into the test piece at various tempera-

tures furnish a means of estimating the rate of softening as the temperature rises. Some clays show a steady progression of softening until complete fusion is reached; others soften somewhat at low temperatures and then exhibit no marked change until just before complete fusion occurs.

Cyanides.—Hand (*Z. angew. Chem.* **18,** 1098 (1905)), in a study of the cyanide mud obtained by Bueb's method of cyanogen recovery, obtains results which vary considerably from those of Feld (this Journal, **27,** 420 (1905)). The mud is a dark brown mass, consisting of soluble bodies, ammonium ferrocyanide, ammonium sulphate, ammonium carbonate, small amounts of ammonium sulphide and about 0.13 per cent. ammonium thiocyanate; of insoluble bodies, iron-ammonium cyanide, ferrous sulphide, tar, sand, ferric oxide, etc. Cyanogen is present to about 8 to 15 per cent. as Prussian blue; the insoluble iron-ammonium cyanide appears to be a double ferrous and ammonium cyanide, $2NH_4(CN).Fe(CN)_2$. On boiling the mud or adding acid to it, the double cyanide is converted into white insoluble $(NH_4)_2Fe_2(CN)_6$ and ammonia is evolved. The difference between the authors' results and those of Feld (*Loc. cit.*) is claimed to lie in the different methods used for determining soluble ferrocyanide and ammonia.

Distillation.—Schidrowitz (*J. Inst. Brew.* **11,** 125 (1905)) contributes an article on brandy, with special reference to those produced in France. Cognac, the best grade, is double distilled in pot-stills at a very slow rate. Usually three fractions are separated; the first runnings, amounting to about 5 per cent., are added to the next charge; the middle portion, beginning at about 85 per cent. alcoholic strength, is collected until the spirit content falls to 56 per cent., thus averaging 66 to 70 per cent. of alcohol in the total portion. The third fraction averages 20 to 25 per cent. alcohol and is rectified by itself or is added to the next charge of wine. Newer forms of rectifying stills, by which the brandy is produced in one operation, are displacing the pot-stills. The author restricts the name "brandy" to a "spirit distilled in France, and the volatile constituents of which are all derived from the grape, and to which only water, sugar and a little coloring-matter may have been added." The analysis of brandy as a basis of determining the genuineness of a sample is to be employed with caution and any attempt to base judgment on the proportion of esters present is declared misleading. Schidrowitz and Kaye (*J. Chem. Ind.* **24,** 585 (1905)) contribute an article on the chemistry of whiskey, with special reference to the product made in the pot-still. The authors were at first inclined to attribute much of the flavor of such whiskey to a kind of dry distillation of the solid matters in the still, consisting of certain woody or cellulose matter from the grain, and of the yeast. They tried destructive distillation

of the yeast and obtained products similar to those derived from the distillation of bones; *i. e.*, amines, bodies of the pyridine and pyrrol class, phenols, nitriles, sulphur compounds, ammonium salts and gases—such as carbon dioxide, sulphur dioxide and hydrogen sulphide. Tests of new pot-whiskey showed evidence of the presence of pyrrol, phenols, hydrogen sulphide, sulphurous acid and an alkaline body, probably ammonia. Attention is directed to the fact that bodies such as these would tend to become altered in time by exposure to air and damp. Thus an explanation of the effect produced by ageing on the crude spirit may be deduced and the elimination of the raw and unpleasant flavor of new pot-still spirit be accounted for. These substances were, however, detected in a whiskey distilled by steam, a fact which led the authors to decide that the bodies were formed in drying out the malt in the kiln and did not have their origin in the still. The results of analyses of malts and grain whiskey are tabulated.

Electric Furnace Products.—Harboard, in the report of the Canadian Commission appointed to examine electrical processes for making iron and steel (*Electrochem. Ind.* 1904, p. 479), states that steel equal to the highest grade of Sheffield crucible steel can be produced at a lower cost by the processes of Kjellin, Keller and Héroult, but that these cannot compete with the Siemens or Bessemer processes for ordinary grades of steel. The reactions in the electric smelting of iron are similar to those in the blast-furnace, and any grade of gray or white iron can be made by suitable changes in the charge and temperature; further, these changes can be made more quickly than in the blast-furnace. But only under the exceptional conditions of cheap electrical power and costly fuel can pig-iron be made electrically to compete with blast-furnace pig. Haanel, in the same report, has a more favorable opinion of the future development of the electric furnace for smelting. Improved forms of furnace with lower cost of electrical energy, and possibly the use of coke from peat, or charcoal briquettes from saw-mill refuse, may reduce the cost materially. The electric furnace, owing to its high temperature and easy regulation, should also be made useful for smelting other ores than iron.

Electro-Chemistry.—Raschen and Clayton (*Eng. Pat.* No. 2152 of 1904) have devised a cell for making metallic sodium by the electrolysis of fused caustic soda. The anode is a sodium-lead alloy; the cathode is a hollow cylinder of nickel and has suspended from its top an iron or nickel annular diaphragm, forming an annular space between them which is closed at the top. The sodium collects in the annular space and overflows through suitable openings into a space at the bottom of the hollow cathode, from which it can be dipped out without admitting air to the interior of the cell. Petit has taken a French patent (No. 353,467)

for the electrolytic reduction of the lead oxide produced in the manufacture of nitrites by reduction of the nitrate with metallic lead. The oxide, suspended in sodium carbonate solution as a thin paste, is spread upon the metal cathode in a closed vessel. The anode is of sheet iron, perforated and arranged to permit the oxygen gas to pass into a receiver. The metallic lead thus reduced is returned to the nitrite process. LeBlanc and Cantoni (*Z. Elektrochem.* **11,** 609 (1905)) have devised an experimental cell of the Castner alkali type, suitable for laboratory work. With a current density on the (mercury) cathode of 0.1 ampere per square centimeter, and the mercury kept in motion, and a highly concentrated potassium chloride solution, the current yield at 40° C. may be above 90 per cent. Gilchrist (*J. Physic. Chem.* **8,** 539 (1904)) found that aniline black was produced at the anode when aniline was electrolyzed in either hydrochloric or sulphuric acid solution. The decomposition potential of aniline was the same (0.95 volt) in both acids, and less than that of either acid alone; thus the oxidation yields the same product in both cases. But hydrobromic acid requires only 0.75 volt for decomposition, hence when dissolved in this acid, bromine derivatives of aniline are produced, notably *s*-tribromaniline. Müller and Spitzer (*Ber.* **38,** 778 (1905)) have repeated the experiments of Traube and Biltz (*Ibid.* **37,** 3130 (1904)) upon the electrolytic oxidation of ammonia to nitrite. Although better yields of nitrite were obtained than by the previous experimenters, the cost appears still too great for industrial application of the process. Traube (*Ibid.* p. 828) replies to the statement of the authors and calls attention to his own prediction that better yields of nitrite could be obtained by adding alkali during the process. An ammoniacal copper solution containing fixed alkali absorbs oxygen from the air more rapidly than when alkali is omitted. Stavenhagen (*Ibid.* p. 2171) has experimented on the oxidation of nitrogen by the high tension spark discharge in a porcelain tube, through which the air is passing. Indications of certain nitrogen oxides formed, which were not caught by the absorbing media, were several times observed. Perkin and Low, in a paper before the Faraday Society, have continued their work upon the electrolytic oxidation of organic compounds of the benzene series, this time having experimented upon ethylbenzene, cumene and cymene. Alcohols and some aldehydes were produced in each case and the authors incline to the view that the hydroxyl ion is the oxidizing agent.

Electro-Metallurgy.—Burgess (*Electrochem. Metal. Ind.* **3,** 17 (1905)) reports investigations on zinc coatings upon iron. Comparative tests between galvanized and electrolytically coated plates were made with $^2/_3$ N sulphuric acid as corroding agent. The resistance of the electrolytically deposited zinc to this acid was much greater than that of zinc applied in the fused bath;

12 grams per square foot of electrically deposited zinc proved equal to 28 grams per square foot deposited from the fused bath. Electrical galvanizing is rather slow and the best coating results with a current of 14.4 amperes per square foot. If the coating exceeds 30 grams per square foot, the surface layers are crystalline and rough. The solutions should be nearly neutral for good deposits, as free acid affects the current efficiency and the quality of the deposit. It is further found that no alloy forms between the iron and zinc in either process; the two metals remain separate. Edison (*Eng. Pat.* No. 26,947, 1904) proposes to clean the surface of metal articles by making them the cathode in a bath with a carbon anode. The hydrogen generated on the metal surface carries away mechanically any dirt, scale or other matter, leaving a clean surface upon which a metallic coating may then be deposited. The process is designed particularly to prepare long strips of sheet iron for nickel-plating. A 10 per cent. solution of potassium cyanide is the electrolyte. Engelhardt (*Stahl u. Eisen*, **25,** 148 (1905)) gives a description of the Kjellin furnace for the electrical production of steel, and compares this method with other steel-making processes. Basing his figures on a cost of 2 pfennigs per kilowatt hour, for electrical energy, the author estimates the cost of fine special steel at 18 to 22 marks per ton by this process, as against 20 to 40 marks per ton by the crucible process. For Martin steel the cost is figured in detail at 68.06 to 71.42 marks per ton, against 75 to 80 marks by the basic process and 85 to 88 marks by the acid process.

Explosives.—Thomson (*Report of Chief Inspector of Explosives*, 1905) describes an explosion of 400 pounds of dry collodion due to collodion dust on the brass runs and guides in the dry room, being fired by friction of the zinc tray on the runs. The collodion contained only 10.61 per cent. of nitrogen, yet the explosion was violent. As a preventive of future trouble in this way, it is suggested that the sliding trays be abolished in the dry room, and that the use of apparatus be avoided in which there are corners where the collodion dust can accumulate. Further, in a report on an accident at Newcastle, Emlyn, Thomsen attributes the explosion to the fall of some iron or steel article on the concrete floor of the storage vault, by which a few grains of powder, accidentally spilled on the floor, were ignited. A lead or linoleum floor covering is recommended. Hake (*J. Chem. Ind.* **23,** 915 (1905)), from an examination of the parchment paper used for wrapping nitroglycerol explosives, through which the nitroglycerol had exuded, concludes that the porosity of the paper was due to an admixture of ground wood, which became charred in the acid of the parchmentizing bath and thus left minute holes in the paper. Lignocellulose was found in the paper. A report upon an explosion in a fireworks factory near Manchester, England, by Major A. Cooper-Key, Inspector of Explosives, gives the re-

sults of certain experiments with a mixture of potassium chlorate, copper oxychloride, arsenic sulphide, potassium nitrate, and rosin. This mixture can be fired by friction between wooden surfaces and is sensitive to blows. It is supposed that two copper funnels, used in filling the mixture into the cardboard cylinders, may have been struck together, or possibly a little grit was present. The inspector recommends that the workmen should wear uninflammable clothing and should not turn up the sleeves while at work. Also that the buildings should have ample means of egress and escape in event of danger. Hake and Lewis (*J. Chem. Ind.* **24,** 374 (1905)) have studied the formation of sulphuric esters in the nitration of cellulose and also their influence on the stability. Two samples of cotton, one suitable for making guncotton, and the other for making blasting gelatin, were nitrated with acids as used in a factory for making nitroglycerol. The temperature of nitration was 73° F.; the samples were soaked one hour in the acid with regular stirring, then the acid squeezed out and the samples washed twice a day for fourteen days in rain-water; after saturating with water, the samples were put into bottles. After several days, the water was tested for sulphuric acid with barium chloride. After again washing for four hours, in running water, the cotton was bottled, kept standing two days more and the water again tested. No sulphuric acid could be detected. After two months the tests were repeated and in nearly every case free acid was found, which was quantitatively determined, and ranged from 0.79 to 0.22 per cent. sulphuric acid in the cellulose. Various solvents were tried with a view to remove the sulphur compounds, and the guncotton then subjected to heat tests (*i. e.*, exposure to a temperature of 170° F., with potassium iodide paper) and to stability tests (heating to 130° C.). The results proved that the sulphuric esters were present in all cases and these decompose slowly during the washing and storage of the wet samples. This free acid then causes erratic behavior in the apparently stable guncotton. It is suggested that this may explain some of the mysterious explosions of guncotton in storage, *e. g.*, that at Stowmarket in 1871. A lengthy discussion of the paper is included. Nauckhoff (*Z. angew. Chem.* **18,** 11, 53 (1905)) has studied the conditions governing the freezing of nitroglycerol and explosives of which it forms a component. A pure nitroglycerol can be chilled much below its normal freezing-point without solidifying, but the true freezing-point is 12.3° C.; commercial nitroglycerol contains some dinitroglycerol which lowers the freezing-point to 10.5° C. This lowering of the freezing-point is expressed by Raoult by the formula $\Delta = E.\frac{m}{M'}$, where 100 grams of the solvent (nitroglycerol) contain m grams of the impurity, M is the molecular weight, and E, a constant, which, for nitro-

glycerol, is 70.5. Additions of benzene, mono-, di- and trinitrobenzene, *o*- and *p*-nitrotoluene, dinitrotoluene, naphthalene and nitronaphthalenes, ethyl acetate and nitrate and methyl alcohol, to nitroglycerol, were found to lower the freezing-point in accordance with the amount calculated by the formula, except that methyl alcohol caused less depression of the congealing point than the formula would require. This is supposed to be due to the formation of more complex molecules in the solution. In general, the effect of a substance in lowering the freezing-point depends on its molecular weight and not on its composition or freezing-point. Tests with dynamite samples showed that the effect of cold is influenced by the amount of cooling below its true freezing-point which the nitroglycerol permits without congealing. This property is affected by the plasticity of the explosive, which, in turn, depends on the proportion of nitrocellulose present and on its gelatinizing properties. Dynamite which has once been frozen and thawed will not withstand chilling to so great a degree as in the first instance. Whatever is added to nitroglycerol to lower the freezing-point must not reduce the explosive power or stability of the explosive, must not be volatile at high atmospheric temperatures, should have a relatively low molecular weight and not affect the gelatinizing of the nitrocellulose.

Brewing.—Windisch and Röttgen (*Z. Untersuch. Nahr. Genussmittel*, **9**, 129 (1905)) have examined the effects of "fining" agents, like isinglass, gelatin, egg-albumen and "Spanish earth" (a China clay) on wines. The ash, extract, and total acidity were not affected; the tannin of red wines was diminished but in one white wine it was increased, for no apparent reason. Spanish earth containing calcium carbonate may reduce the acidity. Keil (*Woch. Brau.* **22**, 432 (1905)) publishes the average alcohol content for certain German beers tested during two years past. Of 476 samples of bottom fermentation, 79.7 per cent. of the pale beers and 71.6 per cent. of the dark beers ranged from 3 to 4 per cent. by weight; the average for the pale beers was 3.55 per cent. and for the dark was 3.70. Top fermentation beers showed much more variation but 112 samples ranged, for the most part, from 1 to 3 per cent. Rogers (*J. Inst. Brew.* **10**, 528 (1904)) considers the proper standard of hard water for pale ale to have the following composition (grains per gallon): Calcium sulphate 60; magnesium sulphate 10; calcium and magnesium carbonates 20; sodium chloride 4; total salts 94. An excess of magnesium sulphate may be compensated by adding calcium chloride. If nitrates are present in the water, it is recommended to add sulphurous acid and boil. Gypsum and potassium salts, as kainite, are desirable for mild ales. Lindet and Marsais (*C. R.* **139**, 1223 (1904)) have fermented equal volumes of sterilized must with equal quantities of the same yeast, and have determined the

quantities of alcohol and carbon dioxide formed at different periods. During the early stages of the fermentation the amount of alcohol is larger than that of carbon dioxide, but later they are practically the same. It is believed that the excess of the alcohol over the carbon dioxide is due to the growth of the yeast itself and the formation of new cells, this taking place chiefly during the early stages of the fermentation.

Fermentation.—Jensen (*Centr. Bakt. Parasitenk.* **13,** 161, 291, 428, 514, 604, 687, 753 (1904)) contributes a long series of articles upon the volatile acids in cheese and the biology of cheese ferments. In some cheeses, volatile acids not produced by hydrolysis were found. Acetic acid was present every time and also formic acid, though only in traces. In cheeses ripened by mold action, small quantities of acetic and formic acids are present along with the acids from the hydrolysis of the cheese fat. The molds cause hydrolysis but not fermentation. In others, propionic acid is found. The acids produced from the cheese fat by hydrolysis influence the aroma, the more so the greater the weight of the acid; thus capric, caprylic and caproic acids have greater influence than valeric and butyric acids. Ammonia is generally found in cheese where hydrolysis of the fat occurs. The peculiar aroma of certain cheeses is due to special constituents: amino-acids in Emmenthaler; butyric esters in Roquefort; putrefactive products in Limburger. Stoklasa (*Chem. Centr.* **1,** 265 (1905)), in a study of anaerobic respiration, found a greater amount of sugar decomposed than was required by the amounts of alcohol and carbon dioxide produced, but an increase of acidity, due to lactic acid, resulted. An enzyme causing this was isolated, and it appeared that when the fermentation continued more than twenty-four hours there was an evolution of hydrogen. The alcohol is oxidized by certain enzymes to acetic acid, while formic acid is also made, and this splits off carbon dioxide and hydrogen. It is thought that this nascent hydrogen has some part in the assimilation of carbon dioxide in the cells having chlorophyll. Ehrlich (*Z. Ver. deutsch. Zucker-Ind.* (1905) p. 539) has investigated the origin of fusel oil in fermentation of saccharine solutions and concludes that it is derived from albuminoid matter in the wort by the action of yeast. This view was advanced by Müller in 1857. The fermentation amyl alcohols are produced from leucine and isoleucine or other amino-acids, as was demonstrated by adding these substances to a pure sugar solution and fermenting; the control test showed only a trace of fusel oil, but that produced in the direct experiments was about equivalent to the quantity of amino-acid destroyed. Leucine produced inactive amyl alcohol and isoleucine formed *d*-amyl alcohol. The small quantities of amino-acid bodies present in yeast account for the production of a little fusel oil when fermenting pure sugar. It is supposed

that the amino-acid unites with the water and then, under the action of the enzymes in the yeast, ammonia is produced and a hydroxyl acid which splits into amyl alcohol and carbon dioxide. Possibly isobutyl alcohol comes from α-aminoisovaleric acid, and *n*-propyl alcohol from glutamic acid. Dawson (*J. Inst. Brewing*, **11**, 288 (1905)) discusses the mechanism of enzyme and ferment action; the action of enzymes is essentially like that of catalytic substances, but their functions are not simply a contact. The enzyme combines with the body on which it exerts its action and the intermediate body formed then breaks up. The law of mass action really controls each of the changes. Hydrolysis by enzymes is due to hydrogen ions to which the compound of the enzyme and original substance is very sensitive. Lange (*Z. Spiritus-Ind.* **28**, 341 (1905)) advocates the addition of formic acid to distillery mashes already sour with lactic acid. This stimulates the fermentation, keeps the diastase active during fermentation, and prevents the action of acid-forming bacteria. Thus the yield of alcohol is increased. The fermentation in the presence of formic acid is quiet and uniform; the secondary fermentation is usually vigorous. The uniform intensity of the fermentation permits filling the vats to a higher level. To 3000 litres of mash about 50–60 cc. of formic acid are used, the strong acid being diluted 1 : 8 with water. The yeast and mash are prepared in the ordinary way and when cooled to 37–38° C. the diluted formic acid is added, 100 cc. to each 100 litres of mash. After three fermentations with yeast, the amount of formic acid is raised to 200 cc. per hectolitre and kept there for six more fermentations; finally 300 cc. acid to each 100 litres of mash are used for continuous work. Emmerling (*Ber.* **38**, 953 (1905)), in further investigation of fermentation of molasses (this Journal, **27**, 434) by the bacteria in potato skins, found the total quantity of alcohols produced was 4.3 per cent. of the molasses (equal to 8.9 per cent. of the sugar). The alcohols consisted largely of ethyl alcohol with *n*-propyl alcohol in small part; *n*-butyl alcohol formed the larger part while little or no amyl alcohol was produced. Exclusion of air furnished the best condition for the fermentation, but this is not absolutely necessary. The bacteria cause liquefaction of gelatine and ferment cane-sugar solution, producing the same alcohols and evolving carbon dioxide and hydrogen. But if calcium carbonate is present, most of the sugar forms fatty acids, especially butyric and a little acetic. The bacteria also ferment maltose, glucose and glycerol, but not lactose. Buchner and Meisenheimer (*Ber.* **38**, 620 (1905)) have continued their investigation of alcoholic fermentation by expressed yeast cell-juice (this Journal, **27**, 432) and confirm their former conclusions that the change of the sugar takes place in two stages, with lactic acid as an intermediate product. They propose to restrict the name zymase to that enzyme which con-

verts the sugar to the lactic acid, and to give the term "*lact-acidase*" to that which changes the lactic acid to alcohol and carbon dioxide. Addition of excess of sugar or of lactic acid seems to disturb the process and destroy the lactic acid produced. Cell-juice of low fermentative power seems to favor the destruction of lactic acid; strong and active juice shows an increase of lactic acid after the fermentation. The inactive form of lactic acid was always produced. Acetic acid is always found in small quantities in the products of cell-juice fermentation of sugar. Warcollier (*C. R.* **141,** 405 (1905)) finds that bruised spots in unripe apples contain starch which remains unsaccharified even after the fruit has become wholly ripe. The tannin which exudes from the damaged cells exerts a paralyzing action on the diastase, thus preventing conversion of the starch to sugar in the ripening process. It was found that 0.2 per cent. of tannin from galls, or 0.075 per cent. of the apple tannin, would prevent the conversion of a 1 per cent. starch paste to sugar, when treated with a 10 per cent. malt extract, at 62° C. Pringsheim (*Ber.* **38,** 486 (1905)) has confirmed Emmerling in regard to a bacillus infecting potatoes and causing the formation of fusel oil in fermentations (this Journal, **27,** 434). Schönfeld (*Woch. Brau.* **22,** 79 (1905)) has continued his study of the effect of metals in causing turbidity in beer, and finds that aluminum in contact with copper causes beer to become turbid by precipitation of albuminoid matter.

Fine Chemicals.—Askenasy and Mugdan have patented (*Eng. Pat.* No. 18,602 of 1904) a method for making acetylene tetrachloride by passing acetylene and chlorine into antimony pentachloride which is well cooled. The gases are passed successively or simultaneously into the pentachloride, which in the latter case is contained in two connecting vessels. The first product is $SbCl_5.C_2H_2$, which then absorbs four atoms of chlorine to form the tetrachlorethane or acetylene tetrachloride. The product is separated by fractional distillation, or in some cases by decomposing the antimony pentachloride with water or acid. The acetylene tetrachloride is a good solvent for fats, oils, etc. Knoevenagel (*Eng. Pat.* No. 23,578 of 1904) makes perfumes by treating condensation products of citral and acetone, acetylacetone, etc., with hydrogen halogen acids, as hydrobromic, in glacial acetic acid; the addition products so formed are boiled with dilute alkali solution to cause the halogen acid to split off, forming odoriferous substances. Hooven and Endemann (*U. S. Pat.* No. 783,524) propose to make cream of tartar by extracting grape pomace with oxalic acid solution. The conversion of calcium tartrate into cream of tartar by boiling with oxalic acid solution and a potassium salt, is included in the claim. Morel (*J. Pharm. Chim.* **21,** 177 (1905)) has an illustrated article upon the commercial manufacture of formaldehyde by passing wood alcohol

vapors mixed with air, over copper at a red heat. The mixture of methyl alcohol, water and formaldehyde is rectified in a column still and a 40 per cent. formaldehyde solution is produced. Reuter (*Pharm. Jour.* **74,** 787 (1905)) proposes to use sulphur dioxide to counteract the tendency of crystallized carbolic acid to turn red in color. Liquid phenol with 10 per cent. water is treated with sulphur dioxide until the phenol has absorbed about 10 per cent. of its weight of the gas. Then a small proportion of this solution (averaging about 50 cc.) is added to 200 kilos of melted phenol. This is said to preserve the phenol from the oxidizing action of the air for a very long time. But as the red color has no injurious effect on the phenol for medicinal use, the author calls attention to this color as tending to prevent mistakes and even suggests adding some dyestuff to the carbolic acid intended for retail trade, and deprecates any use of decolorizing agents. Moissan (*C. R.* **140,** 1209 (1905)) has found that carbon dioxide (dry) and potassium hydride reacting at 54° yield only potassium formate; but if the reaction starts at a temperature between 80° and 200°, a mixture of formate and oxalate of potassium results; thus $2KH+2CO_2=K_2C_2O_4+H_2$.

Foods.—Just (*U. S. Pat.* 789,858, also *Scient. Am. Sup'l.* 1905) prepares milk powder by rapidly evaporating a partially pepsinized milk at 100°, upon the surface of steam-heated rolls, the dry film being automatically scraped off from the rolls by a knife blade. The bleaching of flour by ozone has received further investigation by Brahm (*Z. Untersuch. Nahr. Genussm.* **8,** 669 (1904)) who finds the quality of the flour for bread-making much injured, thus supporting the views of Balland (see review in this Journal, **27,** 429). Roberts (*Eng. Pat.* 23,576 of 1904) restores certain ingredients to flour which have been lost in the milling process, by adding small quantities of potassium, sodium, calcium, and magnesium phosphates and a little soluble proteid as powdered milk proteid. Thorpe (*J. Chem. Soc.* **87,** 206 (1905)) has investigated the effect of souring of milk on the results of the analysis for determination of quality in connection with control under the Food and Drug Acts, in England. Since nearly all the samples sent in for test are sour by the time they reach the laboratory, it becomes necessary to determine the effect of such change. The fat content does not appear to alter to any appreciable degree; nor does the proteid content suffer any considerable loss, beyond the formation of ammonia to a small extent. But the formation of each molecule of butryic acid from the lactic acid causes two molecules of carbon dioxide and of hydrogen to escape as gases. As the lactic acid is oxidized, acetic acid is formed and one molecule each of water and carbon dioxide are evolved. Any ethyl alcohol produced is also accompanied by loss of carbon dioxide which may amount to $^{90}/_{46}$ of the weight of the alcohol so formed. A scheme of analysis as fol-

lowed in the Government laboratories is given. Bodner (*Analyst*, **30**, 264 (1905)) warns against the use of zinc sulphate and potassium ferrocyanide in clarifying wines, owing to the danger in adding either in slight excess. Certain Moselle wines were found thus contaminated.

Gas.—Le Sueur has patented a process (*U. S. Pat.* No. 781,009) for treating acetylene by refrigeration at atmospheric pressure, whereby it is liquefied or solidified, thus facilitating its transportation and storage. Bone and Andrew (*J. Chem. Soc.* **87**, 1232 (1905)) have continued their researches upon combustion, extending their work to acetylene. The combustion of this gas seems to be essentially similar to that of ethylene, ethane and methane. Oxygen appears to combine with the hydrocarbons, forming an unstable molecule which then rapidly decomposes into simpler bodies. Mixtures of acetylene and oxygen filled into glass retorts and sealed under atmospheric pressure, when heated, begin to react at about 250, °and the process advances rapidly at 300°. With mixtures of one to two molecules of acetylene to one molecule of oxygen, explosions take place at 350° and at 375°, when the proportion is two of acetylene to three of oxygen. Excess of oxygen over the equimolecular proportion retards the rate of combustion both below and above the ignition point. The formation of carbon monoxide and hydrogen when the equimolecular mixture is exploded, is attributed to the secondary decomposition of the hydroxyacetylene first produced. In the slow combustion of acetylene, carbon monoxide and formaldehyde are produced at a very early stage, owing to the breaking up of the unstable hydroxyl compound. The following stages of the process are proposed:

$$\underset{}{HC:HC} \rightarrowtail \underset{2CO+H_2}{(HO)C:C(OH)} \rightarrowtail \underset{CO+H_2}{CO+H.CHO} \rightarrow \underset{CO+H_2O}{H.COOH} \rightarrow \underset{CO_2+H_2O}{HO.COOH}$$
$$(1) \qquad (2) \qquad (3) \qquad (4)$$

Below the ignition point in stages (3) and (4) the formic and carbonic acids are split into steam and carbon oxides; and above this point in stage (2) the formaldehyde breaks down to carbon monoxide and hydrogen. This may also happen in stage (1) where the dihydroxyacetylene is formed as an unstable body. Separation of carbon in the explosion of mixtures of acetylene and oxygen does not take place unless an excess of acetylene is present. Contact with a hot catalyzing surface (as porcelain) causes acetylene to unite with water vapor to form acetaldehyde,

$$HC:CH+HOH=CH_2:CH(OH)=CH_3.CHO.$$

Nothing to indicate the formation of benzene was noted in the experiments. Lewes (*J. Gas Lighting*, **89**, 161 (1905)) discusses the theory of the incandescent mantle and inclines to the catalytic theory. The fact that a mantle once brought to incandescence can be kept there by the action of a cold stream of coal-gas with

air, shows catalytic action on the part of the ceria of the mantle. The author regards Buntes' experiments with a Bunsen flame and with a mantle as misleading, since the temperatures in various parts of the flame are changed when a mantle is placed over it. The non-conductivity, low specific heat and low radiation of thoria cause it to take on the temperature of the flame and it may rise a little above this, owing to the catalytic action of the mixed gases. Ceria has greater catalytic power, and in quantities up to 1.5 per cent., tends to localize the combustion on the mantle surface, and thus the ceria particles themselves become much hotter than the mantle. More ceria than this cools the mantle and flame by greater heat radiation, and there is a resulting fall in illumination power. King (*J. Gas Lighting*, **88,** 839 (1904)) compared the results obtained at Cleethorpes, Rushden and Higham Ferrers Gas works, with the water-gas produced by the Dellwik process. The "blue" water-gas is passed through retorts during the carbonization of the coal. The results of eighteen months working at Cleethorpes fix the cost per 1000 cubic foot of water-gas at 3.50d. Water-gas constitutes about 22 per cent. of the mixed gas produced. The quantity of benzene used for enrichment has decreased from 0.38 gallon per 1000 cubic foot, in July, August and September, 1903, to 0.0066 gallon during the same months in 1904. In 1903, the water-gas formed 12.6 per cent. of the mixed gas, which had a candle-power of 16.4 and a calorific value 625 B. T. U. Later, the candle-power was 15.9 and the proportion of water gas 21.3 per cent., with a calorific value of 595 B. T. U. The coal gas furnishes all the enrichment now, and about 400 cubic feet per ton increase of yield is noted. The tar is of slightly lower value. At Rushden, the results agree closely with the above; the yield of coal-gas is about 11600 cubic feet per ton, and the benzene consumption is 0.292 gallon per 1000 cubic foot of water-gas. The mixed gas is 16 candle-power. An extended review upon gas as a source of power appears in *J. Chem. Ind.* **24,** 592 (1905) under the heads: Generation of Producer, Mond and Blast-Furnace Gases (W. I. Case), Utilization of Gas from Suction Producers (Oskar Nagel), Coke Oven Gas (C. G. Atwater), and the Mond Producer (J. D. Pennock). Douglas (*Inst. Mining Metal.*, 1905) considers the use of wood-gas for power, basing his paper upon data obtained from the plant of the Montezuma Copper Co., Sonora, Mexico. The gas produced in modified Loomis-Pettibone apparatus has a calorific value of 135.6 B. T. U. at 62° F. Its composition is hydrogen, 19.5; carbon monoxide, 13.45; methane, 2.48; olefines, 0.34; carbon dioxide, 15.45; oxygen, 0.25; nitrogen, 48.5 per cent. (this Journal, R. 573 (1905)).

Illumination.—von Bolton, at the meeting of the Bunsen Society for Applied Physical Chemistry at Karlsruhe in June, presented

a paper on the Siemens-Halske tantalum lamp, which is reported in *Electrochem. Metal. Ind.* **3,** 328 (1905). The preparation and properties of pure tantalum were described in *Z. Elektrochem.* 1905, p. 45. The lamp with tantalum filament is said to have a useful life of 400 to 600 hours, during which it loses 20 per cent. of its candle-power, and consumes 1.5 watts per candle-power; the total life of the lamp may reach 1,000 to 1,500 hours. The consumption of energy is less than half that of the carbon filament lamp for the same useful life. Steinmetz has patented (*Eng. Pat.* No. 26,916 of 1904) the addition of 2 to 3 per cent. of titanium or its oxide or carbide to the ordinary carbon electrode for arc lamps. The vaporized titanium imparts an intense whiteness to the light. Associated with him, Demster and Härden have taken patents for producing titanium-bearing electrodes. (*Eng. Pat.* Nos. 26,915, 26,918 and 26,919 of 1904).

Health and Sanitation.—T. M. Leggè, Medical Inspector of Factories, reports on the "Manufacture of Paints and Colors Containing Lead, as Affecting the Health of the Operatives" (Abstract in *J. Chem. Ind.* **24,** 742 (1905). Inspection of nearly 100 factories shows that the wet process causes about 18 per cent. of the cases of lead poisoning while dry operations, causing dust, produce 72.9 per cent. Boiling of solutions in certain wet methods has made some trouble, owing to the spray projected into the air acting similarly to the dry dust. Processes employing white lead appear to be much more dangerous than those involving red lead, vermilionettes, chrome greens or yellows. Respirators worn by the operatives have numerous objectionable features, and strong exhaust draught away from the workmen appears more satisfactory. Trillat (*C. R.* **141,** 215 (1905)) finds that formaldehyde is present in the fumes of burning sugar, ranging from 0.2 to 5.7 per cent.; there were also 1.0 to 3.0 per cent. phenols; 1 to 3 per cent. of acetic acid; 0.1 to 5 per cent. acetone; 0.1 to 0.5 per cent. of methyl alcohol, and 0.5 to 1.4 per cent. of benzaldehyde. The gases are of an antiseptic character, for by burning 4 to 6 kilos of sugar in a room of 100 cubic meters volume, very resistant germs are killed. Grossmann (*J. Chem. Ind.* **24,** 655 (1905)) describes his method of treating sewage sludge for its disposal and recovery of products, as applied at Bradford, where 16 tons of sludge are handled daily. Sulphuric acid is added to the sewage to precipitate the sludge and the mass filter-pressed, hot; the cake contains about 24 per cent. grease. This cake is distilled in retorts at temperatures from 200° to 900°, steam being introduced during the distillation. The fatty acids and ammonia distilled off are collected in suitable condensers; the residue of free carbon contains 2 per cent. nitrogen and 1 per cent. phosphoric acid and is used for fertilizer. About 25 pounds of butyric acid and an equal amount of other organic fatty acid are obtained each twenty-four hours.

Moore (*Amer. J. Pharm.* **76,** 553 (1904)) advocates his method for destroying algae (green scum) which grows in ponds and reservoirs by the use of copper sulphate, in the proportion of 1 part to 5,000,000. This was found effective in destroying the odor and taste in a reservoir at Winchester, Kentucky, purifying the water in three days. It also prevented the growth of algae in water-cress beds in the Southern States, without injury to the cress. One treatment per annum was sufficient. It is also claimed that 95 per cent. of the micro-organisms in sewage were destroyed by one treatment with copper sulphate. Kraemer (*Ibid.* p. 574) explains the action of copper sulphate in minute quantities in killing algae on the theory that the plants, being unicellular, are entirely surrounded by the copper and the cell functions are thus all affected. Using copper salt in the proportion of 1 part to 100,000 and 1 part to 1,000,000, after forty-eight hours at ordinary temperature, 99 per cent. of micro-organisms were destroyed in the first series and 90 per cent. in the second. Colon and typhoid bacilli were destroyed in four hours at ordinary temperatures when clean copper foil was suspended in the contaminated water. It is proposed to suspend small strips of copper in the water for domestic uses.

Metallurgy.—Burgess (*Electrochem. and Metal. Ind.* **3,** 332 (1905)) considers the action of acids on iron and the use of acid pickle. Although much investigation of the corrosion of iron by acids has been carried on, information on the subject is still deficient, and among the numerous published articles, so many conflicting statements and faulty and incomplete observations appear, that little of real value can be found. Quantitative tests seem to have been much neglected. Information relative to the effect of impurities in the acid on the corrosion is very much desired. The factors which determine why one grade of iron is better than another for a given use, or whether any certain grade of iron should be employed, should be considered. Concerning the use of acid pickles, the author first gives some interesting statistics as to the importance of the industry. Seventy square miles, or 40,000 acres of sheet metal and 60,000 tons of zinc are used annually for galvanizing in this country, and all of this surface must be pickled; even a larger surface of wire is pickled, while stamping, cold rolling, preparation of enameled ware and electroplated surfaces for painting, varnishing, etc., all involve acid pickling as a preliminary. No uniformity of working has been adopted, each operator having his own method. The ideal pickle is defined as one that removes rust and scale, without attacking the underlying metal. For this, acids having maximum solvent action on oxide and a minimum action on iron, are desired. A table is given showing the variety in practice in the operation of pickling solutions for iron, the composition of the pickles and the time required. Extended citations from

published articles and books on the methods of pickling, the composition of the baths, the effect on the iron of "overpickling," the costs of the process and much other information, are included in the article. Shepherd and Upton (*J. Physic. Chem.* **9,** 441 (1905)) have tested the tensile strength of certain alloys of copper and tin as affected by heat treatment. Bronze with 74.87 per cent. of copper was strengthened by heating above 510°, though there was loss of strength by continuing this heating; this increased the ductility. The maximum tensile strength was found in an alloy having 78.81 per cent. of copper and this contained both α- and β- crystals. Shepherd also examined certain aluminum and zinc alloys (*Ibid.* p. 504). The specific gravity of some of these alloys was determined and was found to be unaltered after heating for a week in boiling naphthalene. The curve obtained by plotting the specific volumes of the different alloys shows two branches which intersect near a point representing the alloy having equal proportions of the two metals. The two phases probably consist of solid solutions. When more than 50 per cent. aluminum is present, the alloys solidify above the eutectic point, 381°. An alloy with 40 per cent. of aluminum shows two phases when examined microscopically; the eutectic contains 5 per cent. of aluminum. Zinc can take up 4 per cent. of aluminum in solid solution, but aluminum can dissolve 50 per cent. of zinc. Goldschmidt (*Chem. Ztg.* **29,** 56 (1905)) states that metallic chromium may be precipitated from the solution of the nitrate by contact with metallic zinc for a day or two. The chromium hydroxide also thrown down can be separated from the crystalline chromium by treating the mass with caustic soda. Hutton (*J. Chem. Ind.* **24,** 589 (1905)) has a review of recent advances in the electro-metallurgy of iron and steel. The electro-thermic reduction of iron, electric steel-making and considerations of the Héroult and Kjellin, Keller, Stassano, Girod, Gin and the Schneider furnaces are included. Ward and Dongden (*Ibid.* p. 186) criticize a paper by Hudson (*Ibid.* **23,** 595 (1904)) in which the glazing of certain kinds of silicious irons is attributed to an increase in the percentage of sulphur. They added sulphur as iron sulphide to the melted iron, but glazed iron was not produced; hence they hold that if high sulphur always does appear in the glazed iron, its presence must be due to the same cause as the glazing. Glazed iron is made when the temperature of the blast is high, with an excess of fuel, and when the furnace is running on an acid slag. The authors think the glazing probably due to the silicide of iron produced by high temperature, but under these conditions there may be a tendency for the sulphur to combine with the melted iron. In discussing the paper, Hudson doubted the presence of free silicide of iron in glazed pig-iron, but admitted that silicon plays an important part in giving a glazed fracture which was only observed when

3.5 per cent. silicon was present; iron containing nearly 4 per cent. silicon in solid solution was easily broken and the fractured crystals present shining surfaces. He maintained that the increased percentage of sulphur might account for the glazing. MacArthur (*Ibid.* p. 311) gives a review of the progress of gold extraction by cyanide solution during the past fifteen years. The early experiments and results of the researches by the author with the Messrs. Forrest upon the action of various solvents upon gold, which led up to the discovery of the action of dilute cyanide solution, are most interestingly set forth; also, the influence which the process has had in the gold-producing districts of the world and in chemical manufacture and research with a view to the production of the necessary cyanide. Barnett (*Ibid.* **24,** 832 (1905)) discusses magnalium and other light alloys. Wöhler prepared two magnesium-aluminum alloys in 1866, *viz.*, Al_2Mg and $AlMg_2$, but neither had any practical use, being brittle and easily oxidized. Three of these alloys are now in use: X used for forging and casting where strength is important; Y used for ordinary casting; Z used for rolling and drawing. Care is necessary with all these to avoid oxidation by overheating or agitation of the fused metal, and the working temperatures range from 300° to 360°, the treatment being, in general, similar to that of aluminum. Magnalium has higher tensile strength and works better in the lathe than aluminum, and is less susceptible to dry, atmospheric corrosion than aluminum, copper, zinc or brass. All the alloys contain over 94 per cent. aluminum with small amounts of copper, nickel, antimony, iron and sometimes lead and tin. "Zisium" and "ziskon" are silver-white alloys and very light, *viz.*, specific gravity 2.95 and 3.35 respectively. Ziskon has much the higher tensile strength. Zisium is chiefly aluminum with zinc, tin, and copper and traces of antimony and bismuth. Ziskon is a zinc-aluminum alloy containing about 25 per cent. zinc. Dewar and Hadfield (*Proc. Roy. Soc.* **74,** 326 (1905)) have found the effect of liquid air temperatures on iron and iron alloys is generally to increase the maximum hardness and decrease the ductility to nothing. Soft Swedish iron, after chilling in liquid air, became very brittle and broke readily when hammered. But its hardness, which was 90 by the Brinell hardness test, was raised to 266 at — 182°. But nickel showed an increased tensile strength and ductility when chilled; thus the addition of nickel prevents the iron becoming brittle. Manganese, on the contrary, makes the iron still more brittle. Hofman (*Trans. Am. Inst. Min. Eng.* (1905) p. 811) has studied the decomposition of zinc sulphate by roasting in an electrically heated tube. Using a thermo-electric pyrometer, the lowest temperature of dehydration of the crystals was 263°, but even after forty hours' heating of 2 grams of the salt, 0.24 per cent. of water remained. The last of the water was not given off until the temperature had

risen to 528° where decomposition of the sulphate began. This decomposition became complete at 739° but required considerable time. Basic sulphate was formed to some extent in all trials. The percentage of sulphur eliminated in a given time, with a uniform increase of temperature in several experiments with various depths of charge, is shown by curves. When carbon is mixed with the zinc sulphate, it assists in the elimination of sulphur, with increasing effect until the temperature reaches 528°, at which point reduction to the sulphide becomes noticeable; but the elimination of sulphur by carbon was not complete, some sulphate remaining after the most favorable trials. Attempts to roast blende to form sulphate directly, showed a small yield in every case; only 9 per cent. of the total zinc in raw blende was converted and 16 per cent. in a mixture of blende and pyrites. The temperature necessary for roasting is too high, resulting in decomposition of the sulphate, while much of the sulphur escapes as sulphur dioxide upon oxidation. High temperatures increase the proportion of basic sulphate formed. Hofman and Magnuson (*Trans. Am. Inst. Min. Eng.* (1905) p. 948) have examined the effect of silver on the chlorination and bromination of gold. Alloys of the two metals were exposed to the action of chlorine and bromine waters. The results show a greater extraction of gold from the alloys when the solution of chlorine was supersaturated, containing 2.8 grams chlorine per liter. With less than 2.1 grams chlorine per liter and more than 10 per cent. silver in the alloy, there was marked decrease in the amount of gold dissolved. Bromine water appeared to be somewhat more efficient; with 20 per cent. silver in the alloy, the gold dissolved was only about 1 per cent. under that taken into solution from pure gold. But again, the quantity dissolved decreased rapidly as the amount of bromine in the water was less. From an alloy carrying 30 per cent. silver, bromine water containing 8.97 grams bromine per liter dissolved 97.7 per cent. of the gold, whereas a saturated chlorine water with 2.8 grams chlorine per liter, dissolved only 40.3 per cent. of the gold. Curve diagrams for both solvents are included in the article. Boudouard (*Iron and Steel Inst.* May, 1905) publishes the results of his study of the fusibility of calcium and aluminum silicates and double silicates and calcium aluminates. Various curve diagrams and tables of analyses are included. Szirmay (*Z. Elektrochem.* 11, 335 (1905)) has made tests of the galvanized coating on iron and steel, produced by both the hot method and by electro-deposition. The latter requires less zinc, has better adhesion to the iron and withstands corrosion much better. Neil (*J. Chem. Ind.* (1905) p. 121) reviews the principal methods of recovering tin from waste tin scrap of the tin can industry. Neuhardt's electrolytic process, the caustic soda electrolytic process, the stannic chloride process and the Browne-Neil electrolytic pro-

cess, are all considered. The results shown by Gayley in experimenting with the dry air blast (*J. Chem. Ind.* (1904) p. 1148) have led Boudouard to study the effect of water vapor on the reduction of iron oxides by carbon monoxide and dioxide (*C. R.* **140,** 40 (1905)). By passing the gas obtained by decomposing oxalic acid over ferric oxide, the gas being dry in one case and saturated in the other with moisture at atmospheric temperature, he found that the dry gas has the greater reducing power at temperatures of 400° to 500°, but as the temperature rises, the effect becomes less marked and finally ceases at about 1050°. Thus it is only in the cooler parts of the furnace that more complete reduction of the iron oxide would be expected with dry air blast. Also the reduction of the carbon dioxide by the coke is less marked at this temperature (500°), which may save fuel. Near the tuyeres the water is decomposed into hydrogen and oxygen and there is nothing certain known as to the action of the hydrogen. Gayley (*Trans. Am. Inst. Min. Eng.*, July, 1905) has contributed another valuable article upon the dry-air blast. The data obtained in running the Isabella furnaces from November 1904 to March 1905, are given and support the views held by the author in his earlier paper. (See *U. S. Pat.* No. 779,037, *Eng. Pat.* No. 13,892, of 1904). von Maximowitsch (*Elektrochem. Ztg.* **11,** 165 (1904)) explains a method for electroplating with copper in which heating or stirring the bath is avoided. The anode is placed above the cathode, both being horizontal, and the copper sulphate solution flows from the former to the latter. The solution contains 220 grams copper sulphate crystals and 25 grams sulphuric acid per liter; the current density was 6 to 10 amperes per square decimeter, and the electromotive force 0.8 volt per ampere, with the electrodes 8 cm. apart. By separating the anode from the cathode by silk gauze, the mud is retained in the anode compartment. The copper deposit is said to be bright, smooth and tough.

Oils.—Petrie (*J. Chem. Ind.* **24,** 996 (1905)) contributes the results of a thorough investigation of the mineral torbanite of New South Wales and of the oils obtained from it. The special characteristic of torbanite is the presence of gelatinous algal substances constituting 90 per cent. of the whole organic matter. Thus there is a high ratio of volatile to fixed carbon. The microscopic structure shows the presence of algal cells. The composition of New South Wales torbanite is C, 75.32; H, 12.05; O, 5.49; N, 0.28; S, 0.31; ash, 6.55 per cent. The sulphur is probably derived from pyrites. The ash contains SiO_2, 77.12; Al_2O_3, 20.14; Fe_2O_3, 0.76; CaO, 0.30; MgO, 0.45; P_2O_5, 0.65 per cent. Extraction of the mineral with benzene yielded a liquid which was fractionated into eight groups, from 79–170°, and tests showed these constituents to be saturated hydrocarbons of high boiling-points, mixed with a small amount of other sub-

stances having high specific gravity and refractive index. High-grade torbanite is exported for gas-making; lower grades are destructively distilled for oils, paraffin and ammonia. A crude green oil is obtained which fractionates into naphtha 3 per cent., solar oil 60 per cent., heavy oil 17 per cent. and a residue 20 per cent. These fractions were carefully examined in detail. The crude oil is composed of paraffins and olefins; the latter distills off under 280°, and the paraffin continues to come over up to 400°. The naphtha forms 9 per cent. of the crude and consists of equal parts paraffins and olefines, with boiling-point ranging from 30° to 200°. Solar oil comes over between 200° and 270°, and contains 50 to 80 per cent. paraffins. The heavy oils come over between 270° and about 400°; they crystallize on cooling and in the portion distilling above 300°, the compounds from $C_{17}H_{36}$ to $C_{30}H_{62}$ make up the mass. At the end of the distillation, chrysene appears. Naphthenes are also present in considerable quantities. Weger (*Chem. Ind.* **28,** 24 (1905)) has examined various commercial burning oils and prepared curves showing percentages of the constituents of different boiling-points, of 14 samples of oil. Boiling-points were determined in the continuous distillation apparatus of Frank, the distillation being continued until about 90 per cent. had distilled over. Olefines were determined by the method of Kraemer and Böttcher; the candle-power showed the American oils at a disadvantage compared with several Russian, Galician and German oils. But for whiteness of flame they hold the first place, since the high content of olefins in the other oils reddens the flame. Rakusin (*Chem. Ztg.* **29,** 139 (1905)) has determined the specific gravity of cacao-butter as 0.9702 at 20°. It sinks in castor oil and must exceed the density of the oil at 0.9604 at 20°. Hoyer (*Seifensiederztg.* **32,** 509, 530, 546 (1905)) describes certain improvements in the process of hydrolyzing fats by the use of castor seed extract (this Journal, **27,** 426); this contains the ferment in more concentrated state than in the crushed seeds and, at the same time, reduces the amount of albuminoid matter introduced into the fat to about 10 per cent. of that in the seeds. Thus a purer glycerol solution is obtained. The temperature should be near 23° for oils and only 1° or 2° above the melting-point of the fats. Above 42° the ferment loses strength. The amount of ferment necessary is directly proportional to the saponification value of the fat, and the water present about 35 per cent. of the weight of the fat. An addition of 0.15 to 0.20 per cent. of the weight of the fat, of manganese sulphate solution, is claimed to be an advantage. The mixture is agitated by a current of air. On standing twenty-four hours, about 80 per cent. of the fat is hydrolyzed and after forty-eight hours, about 90 per cent. With the castor seed extract about 0.06 per cent. (on the weight of the fat) of acetic acid is added. On the completion of the hydrol-

ysis, the temperature is raised to about 80°, and dilute sulphuric acid added to break the emulsion. After standing two or three hours, the clear glycerol solution is run off. A claim is made that 95 per cent. of a theoretical yield of glycerol can be obtained, while the fatty acids are practically anhydrous. After removal of the sulphuric acid, the glycerol is evaporated in vacuum stills.

Ozone.—Guarini (*Elec. Eng.*, 1905, April 14) gives a description of the plant for sterilizing water at the Saint-Maur water works of Paris. The de Frise ozonizer is used and 150 cubic meters of water are treated per hour; an output of 1,000 cubic meters per hour would require only 2 or 3 men and about 129 horse-power for generating and pumping. The ozonizers are worked at 2000 volts tension and they are artificially cooled. The cells are semi-cylindrical brass troughs placed horizontally and covered with a glass plate; each is water-jacketed. The trough is divided by transverse partitions of brass, semi-circular in shape with toothed edges, and 60 mm. less in diameter than the trough; they are suspended from the glass cover and are connected to the generators for high tension current, by liquid resistances which serve as regulators to prevent sparking or arcs. The trough is grounded. Silent discharges from the teeth of the brass partitions to the inner surface of the trough, are produced, and through this succession of discharge areas, the air is drawn to form the ozone. The sterilizers are vertical cylinders divided into segments by transverse diaphragms of celluloid, perforated with fine holes. The ozonized air and water flow up through these diaphragms and are mixed. Finally the water is sprayed into an atmosphere of the ozonized air.

Paints.—Vanino and Gans (*J. pr. Chem.* **71,** 196 (1905)) describe phosphorescent sulphides (Bologna phosphorus), made by heating thiosulphates of barium or strontium to about 1300°. The luminosity is increased by adding a little nitrate of thorium, uranium or bismuth to the mass before heating. Formulae for preparing four different masses are given. Germain (*French Pat.* No. 339,180) proposes a suitable mixture of zinc sulphide, zinc oxide and barium silicate (or silicates of aluminum, magnesium or lead) as a base for paints. Morehead (*U. S. Pat.* No. 779,728) proposes to make lampblack by exploding a mixture of acetylene and air (or oxygen), under such conditions that the minimum pressure required for dissociation (about 60 pounds per square inch) is used. Toch (*J. Chem. Ind.* **24,** 527 (1905)) discusses the conditions affecting the painting of the iron work in the New York subway, with some observations on the progressive oxidation of iron under paint. The author holds that paints which are not moisture- and gas-proof should not be used for subterranean work. A dried film of linseed oil, when exposed to moisture forms with it a semi-solid solution similar to soap, and the moisture is carried through to the iron where it

produces oxidation, especially in the presence of carbon dioxide. The hydrolysis of the oil seems to be hastened by the presence of lime, iron, lead and other bases in the paint, where they act similarly to a catalyzer. Tests of the rust beneath the paint showed it to be laminated in alternate red-brown and dark brown layers of constitution $Fe_2O_3.2H_2O$ and $Fe_3O_4.H_2O$ respectively. It is concluded that the rust formed in the subway is probably a mixture of these two, and further, that in places where there is vapor-pressure, condensation and abnormal humidity, a linseed oil pigment paint is useless. An examination of a steel pier at points covered at mean tide, disclosed oxide scales from $^1/_4$ to $^3/_8$ inches thick, produced by progressive oxidation in the salt water.

Paper, Pulp, Etc.—Beadle and Stevens (*Paper and Pulp*, **10**, 69, 105 (1905); *J. Chem. Ind.* **24**, 775 (1905)) have examined different gelatins with reference to their sizing qualities. Sheets of machine-made, laid paper containing one-third linen and two-thirds cotton, were sized in 5 per cent. solutions of the various gelatins at a temperature of 131°. Corrections for unequal absorption were made in proportion as the amount of gelatin in the paper varied from 5 per cent. and then the strength of test pieces was determined. The price of the gelatin was in no way an indication of its true value for sizing, nor was the stiffness of the jelly a sign of the strengthening properties of the size. Gelatines of the lowest grades (glues) gave greater strength to the paper, but the ink-resisting property is indicated to a considerable degree by the stiffness of the jelly formed. Müller-Jacobs (*Z. angew. Chem.* **18**, 1141 (1905)) proposes the use of amides of the higher fatty acids as substitutes for rosin soap in sizing paper. By heating ammonium stearate to 250° with pressure, stearamide is formed. This can be dissolved in soap solution containing a little sodium carbonate, by boiling. The solution becomes milky on dilution, owing to separation of the stearamide in fine suspended form. On adding alum or other metallic salt, the metallic soap precipitates, carrying down the stearamide with it. When thus precipitated in the hollander, on the paper pulp, and later passed through the callender, the stearamide is fused (melting-point 109°), and gives the paper a water-resistant character. Paper sized in this way is claimed to be more durable than ordinary rosin-sized paper. Richard and Jacquin (*French Pat.* No. 348,354) propose to coat paper or other tissues with an artificial silk layer. A film of nitrocellulose is produced on a polished plate of aluminum by dipping in alcohol-ether mixture; this film is denitrated and colored without detaching from the metal plate. The sheet of paper is then cemented to the film with gelatin and the whole then detached and stripped from the metal plate. Using a cotton cloth backing, a fabric is produced resembling goods woven with silk face and cotton

back. Dietz (*Z. angew. Chem.* **28,** 648 (1905)) has worked out a method for utilizing straw for making cellulose pulp by the sulphite process. The high silica content of straw has prevented its use in this way. It is proposed to dissolve the silica with hydrofluoric acid by which the content is reduced from 1.5 per cent. or more, to less than 0.05 per cent. A bisulphite liquor carrying 3.6 per cent. of sulphur dioxide, of which 2.4 per cent. is free, is used in the proportion of 4½ times the weight of the straw. The boiling continues for three hours at 3½ atmospheres' pressure. A yield of 42 per cent. of cellulose is claimed, and this bleaches well with 13 per cent. of bleaching-powder. Sindall (*J. Chem. Ind.* **24,** 770 (1905)) describes the making and use of art papers such as have a very smooth surface for printing from half-tone blocks. The materials used, the qualities desired in the body paper, the defects common to such paper, the influence of the mineral filling on the print, and some suggestions relative to the production of such smooth papers, are the chief points considered. The surface is composed of glue or casein mixed with clay, *blanc fixe*, satin white or other mineral matter; the body paper consists of wood pulp or a mixture of this with esparto fibre. It is suggested, that, as these papers are not very durable, especially when exposed to dampness, the proper storage in a dry room of books made from it, is essential. A surface coating of cellulose in some soluble form is very desirable, but has not yet come into extended use.

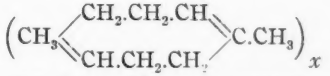
Photography.—Morgan (*Eng. Pat.* 26,247 of 1904) prepares self-toning printing paper thus: For the emulsion, dissolve 6 drams sugar, 5 drams citric acid, 64 grains ammonium chloride and 4 drams Rochelle salt in 24 ounces water, to which has been added 1.5 ounces arrowroot starch. Then add 9 drams 36 grains silver nitrate in 8 ounces water; 11 grains gold chloride in 6 ounces water; 2 drams agar-agar in 18 ounces water. Coat the paper with this emulsion and finish as with a gelatin-coated paper. In this emulsion the gold is more easily reduced in the "hypo" bath. Lumière and Seyewetz (*Monit. Scient.* **19,** 104 (1905)) produced brilliant green tones in the silver image by bleaching in a solution of potassium ferricyanide 60 grams, lead nitrate 40 grams, water 1 liter. After washing, pass the plate into a solution of cobalt chloride 100 grams, hydrochloric acid 300 grams, and water 1 liter. The formation of a double silver-lead ferrocyanide in the first reaction is incomplete and the composition of the image is between $Pb_3Ag_2Fe_2(CN)_{12}$ and $Pb_2Fe(CN)_6$. Part of the lead is then substituted by the cobalt and the composition of the image finally lies between $Co_2Ag_2PbFe_2(CN)_{12}$ and $Co_2Fe(CN)_6$. These authors (*Brit. Jour. Phot.* **52,** 68 (1905)) have toned negatives with salts of uranium, copper and iron in conjunction with potassium ferricyanide, to obtain colored images. These images were of a very complex composition; thus with uranium

the composition appeared to be intermediate between bodies having the formula $Fe.Ag_2UO_2(CN)_6$ and $(FeAgUO_2(CN)_6):UO_2$; the copper image was between $(Fe.Cu.Ag(CN)_6)_2:Cu$ and $FeCu_2(CN)_6$ and with iron it was between $Ag_2Fe_2''Fe_2'''(CN)_{12}$ and $Fe_3''Fe_2'''(CN)_{12}$. Kessler (*Ibid.* p. 28) describes a thiocarbamide toning bath made up of a 2 per cent. solution of thiourea added to 25 cc. of 1 per cent. gold chloride solution, until the precipitate formed at first is redissolved. (This requires about 15 cc.) Then 0.5 gram of citric acid is added and the whole diluted to 1 liter. Brownish red to violet tones are furnished by this bath. Namias (*Ibid.* p. 106) proposes to give a blue color to "bromide" prints by toning with molybdic acid. No silver salt is left in the toned image and it is probable that the silver merely aids the reduction of the molybdic acid. Pure whites cannot be obtained readily.

Pottery.—Edwards (*Trans. Engl. Ceramic. Soc.* **4,** 32 (1903)) has experimented with pure precipitated tricalcium phosphate in the body for china. The ware was as translucent and showed no more fusibility, nor warp, than that containing bone-ash. Adding calcium fluoride to the phosphate appeared to have no effect. Commercial precipitated calcium phosphate in the ware caused it to soften and warp entirely out of shape when fired. This is supposed to be caused by the alkali left in the phosphate by incomplete washing. The view is advanced that in ordinary chinaware about 15 per cent. of the total calcium phosphate serves as a flux and the rest renders the ware white and more translucent. The phosphate, which is uncombined and in excess being infusible, gives the body greater stability at the high temperature of firing. Berdel (*Sprechsaal,* **38,** 345, 393, 438 (1905)) has experimented on the production of non-poisonous lead glazes, which should withstand the test of boiling in a 4 per cent. acetic acid solution for half an hour, and then passing hydrogen sulphide into the liquid, whereby no precipitate should form. Various formulae for colorless, salmon-red, purple, black, green and blue glazes are given, the products of which will stand the above test.

Rubber.—In the *Bull. Imp. Inst.* **3,** 146, 147 (1905) are reports upon the rubber from certain species of *Landolphia* (*L. ugandensis*) from East Africa Protectorate, and that from the *Ficus elastica* from Madras Presidency. The former contained caoutchouc, 78.3; resin, 9.1; moisture, 6.2; insoluble matter (dirt), 6.4; ash, 2.4; the latter contained caoutchouc, 85.2; resin, 7.8; albuminoid matter, 1.4; moisture, 3.7; insoluble (dirt), 1.9; ash, 0.5. Alexander (*Ber.* **38,** 181 (1905)) has attempted to make the dinitro-caoutchouc of Weber from crude rubber, but in no case could he get a product agreeing with Weber's formula, $C_{10}H_{16}N_2O_4$. The products generally corresponded to the "nitrosit C" of Harries, $(C_{10}H_{15}N_3O_7)_2$, though containing more

carbon and less nitrogen than the formula implies. The products thus made from crude rubber are supposed to be mixtures of nitrosit C, with more or less oxidation products, since the lead nitrate on decomposing yields both oxygen and nitrogen peroxide. Harries (*Ber.* **38,** 87 (1905)) has also experimented with nitrogen peroxide upon caoutchouc but failed to form anything corresponding to Weber's dinitro-caoutchouc; the products were nearer the author's nitrosit C, produced when nitrous acid acts on rubber. Both reactions take a somewhat similar course, yielding products soluble in acetone and ethyl acetate, but nitrogen peroxide does not seem to yield a product of constant composition. This casts doubt upon the general accuracy of the "dinitro" method for determining caoutchouc. The author also contributes another article (*Ibid.* p. 1195) bearing on the constitution of caoutchouc. Experiments have been made with the *ozonide*, which, on decomposition with water, gives levulinic aldehyde or acid. This indicates that the caoutchouc molecule is a closed ring, and the molecular weight determinations with the ozonide indicate its formula to be $C_{10}H_{16}O_6$. A formula for paracaoutchouc is proposed, *viz.*:



Burgess (*Chem. and Drug.* **66,** 911) proposes to coagulate the latex of *Ficus elastica* by heating to 40° and adding a 2 per cent. solution of tannic acid. The method is much more rapid than the usual process of exposing to the sun and air.

Starch.—Roux (*C. R.* **140,** 440 (1905)) has succeeded in producing artificial starch by converting amylocellulose into simpler substances at temperatures near 150°. If an excess of water is present, amylocellulose liquefies at 150° and degradation sets in, producing various substances, which are colored blue by iodine but do not form a jelly with hot water. The changes are the reverse of those by which amylocellulose is made from starch-paste and cannot take place if the transformation has gone too far and produced amylodextrin or glucose. The author considers the artificial starches as identical with those from cereals under the same temperature conditions; they are all thought to be more or less condensed forms of the same nucleus. In a later paper (*Ibid.* p. 943) he explains the rapidity of reversion of solutions of these starches on standing at ordinary temperatures, and as compared with that of potato starch. In a 3.3 per cent. solution made by heating ten minutes at 100°, and four minutes at 150°, 43 per cent. reverted within one hour, but in a solution made at 100° only 1.8 per cent. reverted in that time. Acids and bases seemed to accelerate the reversion of the "artificial" starch; 1 per cent. of sulphuric acid caused reversion in five days at 0°. At 100° no reversion occurs in these solutions; the re-

verted product dissolves only at the temperature at which the original starch dissolved. Roux also finds (*Loc. cit.* p. 1259) that "artificial" starch yields 96 to 98 per cent. of maltose when saccharified with malt extract at 56°; ordinary starch under the same conditions yields an average of 82.3 per cent. At 67°, the artificial starch yielded 55.1 per cent. and the ordinary starch only 45 per cent. At 80° malt extract had no action on the artificial starch. In conjunction with Maquenne (*Loc. cit.* p. 1303) the author shows that ordinary starch by the iodine test and also by the saccharification test, contains 80 per cent. of amylocellulose, a body identical with "artificial" starch. The other 20 per cent. consists of mucilage-like substances called amylopectin and to which the gelatinizing of the starch paste is due; this is not present in "artificial" starch.

Sugar.—Ost (*Z. angew. Chem.* **30,** 1170 (1905)) has converted *r*-glucose into *δ-l*-fructose by treatment at ordinary temperature with fairly strong sulphuric acid. By dissolving 1.1 kilos of glucose in a cold mixture of 1 liter of concentrated sulphuric acid with 2 liters water and keeping at room temperature for four months, then neutralizing with chalk and evaporating at very low temperature and adding alcohol and ether, the residual liquors were levo-rotary. From 100 parts glucose, about 20 parts isomaltose, 5 to 10 of fructose and 60 parts unchanged glucose were obtained. From a 10 per cent. syrup the fructose was precipitated at 0° by adding dry slaked lime; the calcium fructosate was thus separated and decomposed with oxalic acid to reform the sugar. It was crystallized by cautious concentration of its syrup and addition of methyl alcohol and ether.

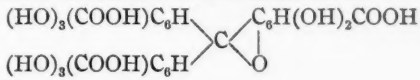
Tanning.—Nierenstein (*Collegium,* **21,** 197 (1905)) has investigated some tannins which cause "bloom" or an efflorescence on the leather. The author holds that this is produced by material present in the tannin substance, partly as a soluble glucoside and partly as ellagic acid, these also having tanning action on the skin. Tanning action is produced by bodies having "tannophor groups," *viz.*, CHO, CO and CO.O. The same writer (*Ibid.* p. 159) contributes some observations on the formation of leather, based on experiments with formaldehyde on skin. By boiling out the leather with water until all formaldehyde was removed and then boiling with dilute sulphuric acid, more formaldehyde was extracted from its chemical combination with the hide. The author proposes two formulae for the reaction of leather-making:

$$\underset{\text{Pelt.}}{RNH_2} + \underset{\text{Formaldehyde.}}{CH_2O} \rightarrowtail \underset{\text{Leather.}}{R.N{:}CH_2.}$$

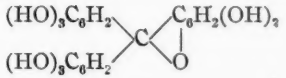
Using vegetable tannin, carrying the "tannophor" CO or CO.O,

$$\underset{\text{Pelt.}}{RNH_2} + \underset{\text{Tannin body.}}{R^2C.O.O.R^3} = \underset{\text{Leather.}}{R.N{:}C(R^2).O.R^3.}$$

In a further communication (*Ibid.* p. 221) the author considers the "tannophor" , reviewing some work of von Baeyer (*Ber.* **25,** 280, 1096) who found that pyrogallol with formaldehyde gave a substance resembling tannin and which precipitated gelatin from solution. The author repeated these experiments and also tried formaldehyde with gallic acid, and got in both experiments soluble substances which precipitated gelatin. The formulae of these substances were established as



from gallic acid, and



from pyrogallol. Both contain the tannophor group: .

Eitner and Stiazny (*Der Gerber,* **31,** 125, 139 (1905)) have experimented with mixtures of salt and acids for pickling skins. Hydrochloric, acetic and lactic acids seem to have no advantage over sulphuric, the leather in all cases being essentially the same in quality. The concentration of the solution affects the quantity of salt taken up by the skins. Larger amounts of acid improved the quality of the leather. Absorbed sulphuric acid even to the amount of 3 per cent. is claimed to produce no tendering of the leather on drying.

Tar.—Loew-Beer (*Z. angew. Chem.* **18,** 8 (1905)) describes a continuous acting tar-still of the Lennard type (*Eng. Pat.* No. 844 of 1891) in an improved form. The still consists of two rows of cast-iron pipe coils, heated by gas or liquid fuel. The cold tar is itself used to chill the first two condensers in which the volatile products are condensed, and it is thus heated to a sufficient degree to expel the ammoniacal liquor and some naphtha. These are condensed in a special cooler. The heated tar enters the pipe coils at the top of the furnace and leaves through the bottom coil, which is at a higher temperature. This hot tar flowing out at near 300° is brought into contact with superheated steam at 300° in the "pitch scrubber," which drives out the volatile products, and the pitch passes on to a collecting tank. The vapors go first to the condensers cooled by the incoming tar and then to others cooled by water. The anthracene oil condenses in the first, creosote oil in the second, and in the water-cooled coils the light oils are collected. The apparatus is worked under a vacuum of 550 mm., with water and oil towers between the

vacuum pump and the condensers, to prevent any loss of volatile substances.

Textiles.—Bernstein has patented a process for artificial silk (*U. S. Pat.* No. 754,027) in which the liquor boiled off from raw silk is mixed with a solution of cellulose in ammoniacal copper hydroxide. The mixture is heated slowly and spun into threads which pass through an acid bath. They may be further softened by passing into a solution of neutral alizarin assistant (Turkey-red oil). Holle (*Z. Farb. Textil-Chem.* **4**, 144 (1905)) has found that cotton fibre is occasionally injured by a fungus, which resembles cellulose in appearance. The fibres attacked showed a darker shade on dyeing than did the normal cotton. The fungus appears to be present in the seed-cells and develops with the new plant.

Miscellaneous.—Griffin (*J. Chem. Ind.* **24**, 183 (1905)) has a thoughtful review upon standard methods of drawing samples for analysis. He shows that, with the exception of a few papers on special cases, little or nothing of value has been published on the subject. Standard methods of analysis of certain classes of materials have been proposed and tested by committees of various societies and associations, but the drawing of the samples has been left to "boys and pensioners" in many cases. The author makes several suggestions looking to improvement in this work, and finally recommends that a few chemists working in similar lines should disclose directions how samples of the materials with which they are familiar, should be drawn. Gardner and Lloyd (*J. Chem. Ind.* (1905) p. 392) have published some "Notes on Water Softening." The subject is considered under several heads: The Effects of Neutral Salts; Influence of the Apparatus; Determination of Lime Factor and of Soda Factor. Neutral salts frequently interfere with complete softening, as the alkalinity then becomes too high. In this case, the use of barium hydroxide to remove sulphates may have some advantage. The time allowed for settling and the temperature at which the purification is carried on are affected by the kind of apparatus used. Agitation after mixing with reagent is an important factor; pressure also seems to assist the completion of the reactions. The formula proposed by Pfeiffer for determining the amount of lime needed to purify a water has been found unreliable for water containing neutral salts. The formula is Ht+Hm—Hp= lime needed, when Ht is temporary hardness, Hp is permanent hardness and Hm is magnesium hardness. But with mixtures of calcium bicarbonate and magnesium sulphate, more lime is needed to remove all the magnesium salts as well as the calcium bicarbonate. Experiments with barium hydroxide lead to the conclusion that it is too expensive except for very special cases, and in the presence of sodium sulphate it is unsuitable since sodium hydroxide remains in the water. A report of the Departmental Committee

on Industrial Alcohol, to the Chancellor of the Exchequer, appears in the *J. Chem. Ind.* **24,** 397 (1905). The uses of alcohol in the arts, the hindrances to the use of spirit for industrial purposes and certain suggestions looking to relief from present restrictions, are included. The entire report, sub-reports and five appendices are too extensive for a satisfactory short abstract. Zalackas (*C. R.* **140,** 741 (1905)) reports that the juice of *Nasturtium officinale* is a positive antidote for nicotine poisoning. The juice usually contains iron and iodine which are supposed to revivify the blood corpuscles that have been poisoned by nicotine. Perkin, *et al.* (*Eng. Pat.* No. 22,169, 1904) propose to render wood fire-proof by treating for six hours at 500 pounds pressure per square inch, with a sodium stannate solution at 32° Bé. or a mixture of sodium stannate and tungstate solutions. After drying by hot air, a solution of ammonium sulphate or zinc sulphate or acetate, or a mixture of zinc sulphate and tartar emetic is applied under pressure. After drying, the wood is washed and is ready for use. Ditz (*Chem. Ztg.* **29,** 581 (1905)) has tried the catalyzing action of rare earth compounds for the oxidation of naphthalene by sulphuric acid to form phthalic acid. The substances used were carbonates, oxalates and hydroxides of cerium, lanthanum, neodymium, praseodymium and yttrium, obtained as residues from the preparation of thorium nitrate. The oxidation began at about 220°, and was completed at 300° when the mass became viscous and decomposition took place. The distillate contained sulphuric acid and phthalic anhydride, but the yield was less and the process not so rapid as with mercury for the catalytic body. Perotti (*Chem. Centr.* **1,** 117 (1905)) shows that calcium cyanamide, when used as a fertilizer, may injure the germinating seeds and otherwise interfere with the growth of the plant. When used, it should be applied to the soil before the seed is sown. The Forty-first Annual Report of the Chief Inspector of Alkali Works in England was issued February 27, 1905. Statistics of the various manufactures coming under the supervision of the inspectors constitutes an important part of the publication. It appears that the new "Alkali Works Bill" introduced in Parliament last year, was subsequently withdrawn, but will be again introduced next session. It is estimated that one-half the world's production of bleaching-powder (260,000 tons) is made by electrolytic processes. In sulphuric acid making, artificial draught and the use of atomized water continue to find more extended acceptance. A plant using the tangential system of chambers, devised by Meyer, has been started. No further extension of contact methods has been noted. Kessler's system of concentration continues to work well. More attention is being given to the production of arsenic-free acid and an explosion of a hydrogen sulphide-air mixture used in this purification, is noted, the cause being given as contact

with iron oxide scales on the inside of the pipe through which the mixture was passing. A lead pipe was later substituted. The evaporation of salt by means of Mond producer gas and the utilization of the vapor from the brine evaporation as the supply of aqueous vapor to the producer, is one of the newer ideas noted. For cement-making, the rotary kiln is finding more extended use. The Höpfner electrical method of extracting zinc from blende is in successful operation at one works. A large part of the report is comprised in a further contribution upon "Studies of the Claus Kiln Reaction," with reference to the "Influence of the Various Contact Substances on the Interaction of Steam and Hydrocyanic Acid."

NEW BOOKS.

THE STUDY OF CHEMICAL COMPOSITION, AN ACCOUNT OF ITS METHOD AND HISTORICAL DEVELOPMENT, WITH ILLUSTRATIVE QUOTATIONS. By IDA FREUND, Staff Lecturer and Associate of Newnham College, Cambridge. Cambridge: The University Press. 1904. 650 pp. Price, 18/ net.

The second part of the title gives a better idea of the scope of this work than the first. It is not so much a treatise on chemical composition, after the manner of the ordinary text-book, as "an account of its methods and historical development, with illustrative quotations." The author disclaims that it is a history of chemistry, yet, while it does not enter into detail as fully as do many histories, the development of the fundamental chemical conceptions of the present day is very fully traced, much more fully and logically than in most histories of chemistry properly so-called. The author quotes very freely from original sources, the experiments of the writers being described and their reasoning given in their own words wherever possible, and this gives to the book a peculiar freshness which will be appreciated by every reader who has felt the advantage of going to original sources rather than consulting reviews, abstracts and restatements. Probably there has never been collected within the same space so many quotations from the fathers of chemistry, perhaps 40 per cent. of the volume of 650 pages being quoted, yet it is by no means a compilation merely, the original matter supplied by the author being also of great interest and value.

In the introduction the author discusses the method of the inductive sciences, observations, generalization, law, theory and hypothesis, using as illustrations the classical experiments of

Lavoisier on the supposed conversion of water into earth, of Davy on the supposed production of acid and alkali by electrolyzing water, and of Rayleigh and Ramsay on the density of nitrogen. In the following chapter the theory of combustion is set forth in the same manner. The discovery of the laws of fixed and multiple proportions is abundantly illustrated, and the theory and practice of the method of determining atomic weights is expounded with numerous quotations from Stas, Morley and other masters. About 30 pages are devoted to a consideration of the various classes of errors to be encountered and overcome in exact chemical work. The law of Avogadro, the periodic law, the doctrine of valency and other important generalizations of chemistry are interestingly treated of by the historical method. Two chapters are devoted to the ultimate constitution and genesis of matter, the former giving the views of the ancients and of the earlier chemists of modern times, especially with reference to the hypothesis of atoms, the latter and concluding chapter of the book dealing rather with more recent speculations, such as those of Prout and Crookes, and the recent researches on radio-activity and the speculations following therefrom.

The author has omitted to deal with the theory of solutions and other important branches of modern physical chemistry, and although this omission is explained in the preface as being due to lack of space and to the existence of many modern textbooks which cover the ground completely, yet we cannot but regret that she has so decided, as these subjects would undoubtedly have been treated in a fresh and original manner and the value of the work for the chemist and especially the general scientific reader would thereby have been increased. In distinction from the rest of the work the chapter on crystallography is more descriptive than historical, which we consider also a defect, as there are numerous books on this subject, but none which adopts as fully the evolutionary method of treatment so successfully followed in this work. With these exceptions the work is almost above criticism. It is earnestly to be recommended to all students of chemistry as a correction to the tendency to too close specialization, and should form a part of every course of chemical reading. Even those familiar with the outlines of chemical history will find it profitable reading. It might also be read to advantage by students of philosophy and others who wish to get an idea of

how and by what methods one of the most important of modern sciences has grown from its earliest beginning, and how difficult it is to arrive at anything like correct views of nature without constant appeal to nature itself.

In conclusion, the reviewer wishes to express the pleasure he takes in the fact that we have at last a chemical treatise by a woman, which shows a high degree of scholarly attainment and originality and which is well worthy to rank with the best known and most used works on the history and philosophy of chemistry.

H. N. STOKES.

ECONOMIC GEOLOGY OF THE UNITED STATES. By HEINRICH RIES, A.M., PH.D., Assistant Professor of Geology at Cornell University. New York: The Macmillan Company. 1905. xxi+435 pp. Price, $2.60 net.

The ground covered by this work is essentially that gone over in the elementary course in economic geology at Cornell University. The presentation of the subject differs from that in most text-books in that the consideration of the non-metallic minerals precedes that of the metallic minerals, this change having been made for the reasons that the production of the former is far in excess of the latter, and that the discussion leads up from the simpler to the more complex forms of mineral deposits. Geologic and physiographic principles are not presented. Brief statistical statements of production will be found of value by the student and lay reader, as also the bibliographical references at the end of each chapter.

W. F. HILLEBRAND.

A LABORATORY GUIDE TO THE STUDY OF QUALITATIVE ANALYSIS, Based upon the Application of the Theory of Electrolytic Dissociation and the Law of Mass Action. By E. H. S. BAILEY, PH.D., Professor of Chemistry, and HAMILTON P. CADY, PH.D., Assistant Professor of Chemistry in the University of Kansas. Fifth edition, thoroughly revised. Philadelphia: P. Blakiston's Son & Co. 1905. Price, $1.25.

Although the entire book has been thoroughly revised, and certain portions of the text rewritten where greater clearness was desired, yet the principal change in the fifth edition of this book is one of arrangement. The entire scheme for the separation of the cations, accompanied by explanatory marginal headings, is placed at the end of the preliminary experiments upon the seven groups. This has the decided advantage of giving a definite, continuous procedure, which may be followed in making a complete separation of the cations, while the reactions dis-

cussed under the individual groups may be easily referred to for confirmatory tests. The analysis for the anions is treated in a similar manner. In this section the division into groups has been slightly altered, and a number of new tests added.

The subject is treated from the standpoint of the Electrolytic Dissociation Theory and the Mass Action Law, which are developed in the first part of the book. M. S. SHERRILL.

BEET SUGAR MANUFACTURE AND REFINING, Vol. I. Extraction and Epuration. By LEWIS S. WARE. New York: John Wiley & Sons. xxvii+543 pp. 262 figures. Price, $4.00.

Notwithstanding the rapid developments of the beet-sugar industry in this country during the past twenty years, those desiring a satisfactory treatise upon the subject have been obliged to consult the various foreign works, such as that of Horsin-Deon in French, or the volumes of Stohmann or Claassen in German. We now have in the forenamed book, Volume I of what promises to be the first complete work in the English language upon the beet-sugar industry. No one is better qualified than Mr. Ware to undertake a task of this kind. As editor of the "Sugar-beet" he has long been prominent in the sugar world, and his numerous visits during the past thirty years to hundreds of beet-sugar factories in various European countries have given him a more impartial command of the subject than the numerous French and German authorities who so frequently argue, to quote from the writer's preface, "from the bias of their respective national standpoints." The book is written entirely from European observations, the author remarking somewhat ironically that he makes no mention of American methods, his "intention being to avoid any attempt at criticising some very glaring blunders."

In Part I of the volume the preliminary operations of beet delivery, siloing, washing, etc., are taken up. Part II is devoted to extraction, and discusses methods of slicing, working of the diffusion battery and the exhaustion and drying of cossettes. Part III, the largest division of the volume, gives eight chapters to the subject of epuration and treats of liming, carbonatation, filtration, and sulphuring. A chapter is also given to the less common methods of clarification. The author's introductory remarks upon practical considerations form one of the best

points about the book. A careful perusal of these 14 pages will cause those inclined to be overzealous to think seriously before embarking upon the beet-sugar enterprise.

A very complete bibliography of the various works and journals consulted is given, and the references made to these in the text are indicated at the bottom of the page. We are glad to see that an index has been provided, the lack of this in the first volume of uncompleted works being often a source of annoyance.

The publishers have performed their part of the work most satisfactorily, the typography and illustrations being excellent. The succeeding volume of Mr. Ware's book will be awaited by the sugar world with great interest. C. A. BROWNE, JR.

TECHNICAL METHODS OF ORE ANALYSIS. By ALBERT H. LOW. New York: John Wiley & Sons. 1905. x+273 pp. Price, $3.00.

This is a book of 273 pages, and according to the preface is designed as an aid "to the technical chemist," but it is hoped by the author that it "may also prove useful to the student desiring to become acquainted with technical methods." Both of these intentions seem to have been quite satisfactorily carried out.

The first chapter of 7 pages describes some special forms of well-known apparatus which the author has found particularly desirable. Following this is a chapter on electrolysis, giving briefly the apparatus necessary to carry on electrolytic methods and the general precautions and procedure required. Chapter 3 is a short one on the use and advantage of logarithms in chemical calculations. Following this is the main part of the book, in which are described methods for the determination and separation of the various metals and elements ordinarily required in metallurgical work, beginning with aluminum and including antimony, arsenic, barium, bismuth, cadmium, calcium, chlorine, chromium, copper, iron, lead, magnesium, manganese, mercury, molybdenum, nickel and cobalt, phosphorus, potassium and sodium, silica, sulphur, tin, titanium, tungsten, uranium and vanadium. These are treated in separate chapters.

Chapter 30 suggests methods for separating the elements when more complete analyses from one sample are desired.

Chapter 31 treats of the analysis of boiler waters, and chapter 32 the analysis of coal and coke. There is also a short chapter on testing crude petroleum.

The arrangement of the matter is excellent, being divided into paragraphs and with many cross references. The directions are in full detail, and the author, by the frequent use of the personal pronoun, shows that he is personally acquainted with the processes described.

The book speaks for itself but the long experience and well-known reputation of the author is sufficient guarantee as to the quality of the matter. It is a book that can be recommended to chemists engaged in the analysis of minerals or metals, and particularly to the student who desires to practice the methods generally adopted in the works laboratories. WM. HOSKINS.

DIE MIKROSKOPIE DER TECHNISCH VERWENDETEN FASERSTOFFE. By DR. FRANZ RITTER V. HÖHNEL, Professor in the Technical High School of Vienna. Second Edition. Vienna and Leipzig: A. Hartleben. 1905. 248 pp. Price, 6 Marks.

This work of Professor Höhnel is a revised and somewhat enlarged issue of his previous volume on the same subject. The microscopy of fibrous materials of technical application is a wide field, and this book is probably the only one of its kind which attempts to treat of the entire subject. The excellencies of Professor Höhnel's earlier edition made it a recognized authority on the subject, and these good features are preserved in the present volume, to which there is also added an additional amount of information resulting from the researches of both the author and other investigators subsequent to the publication of the first edition.

Höhnel's micro-analytical classification of the vegetable fibers is especially valuable, and it is only to be regretted that he has not extended the same method into the study of the animal hair fibers. The consideration of the vegetable fibers occupies the major portion of the book, and the description of the various fibers employed in textiles and in paper-making is very thorough and complete.

The principal features which have been added to this edition are considerations of mercerized cotton and the various forms of artificial silk. A number of new drawings, chiefly the work of cotemporary observers, has also been included. Höhnel's own drawings illustrative of the microscopic appearance of the fibers have become more or less classic. Perhaps these drawings exhibit characteristics which the author desires to emphasize

more clearly than would actual photomicrographs of the fibers themselves; the only criticism that can be offered is that such drawings are apt to be more or less idealized, or rather conventionalized, with the result that unless a person is thoroughly familiar with just what features are to be observed under the microscope, he would experience difficulty in many cases in identifying some of the fibers drawn by Höhnel. Another criticism to be offered is that though Höhnel's book is eminently scientific and must always occupy a high place in the literature of the subject, the technical or practical side of the matter is rather badly neglected, which is rather disappointing in a book purporting to deal with the "technically applied" fibers. To the scientist or advanced student interested in the subject the present volume is what may be termed a valued "classic," but to the purely technical student and the one to whom the volume should make the greatest appeal and be of the greatest utility, Höhnel's book, we fear will be too highly theoretical for practical use.

J. MERRITT MATTHEWS.

A SYSTEMATIC COURSE OF PRACTICAL ORGANIC CHEMISTRY. By LIONEL GUY RADCLIFFE and FRANK STURDY SINNATT. London: Longmans, Green & Co. 1905. xi+264 pp. Price, $1.40.

The systematic course (96 pages) begins with methods for the detection of the various elements present in organic compounds; the determination of melting-point, boiling-point, and specific gravity; the purification of organic substances (crystallization and sublimation); and the determination of molecular and equivalent weights. This introductory portion (22 pages) is followed by detailed descriptions of the preparation of various typical organic compounds, accompanied by numerous experiments illustrating their characteristic reactions. These preparations and experiments are so arranged as to follow along with the lectures on the theoretical side of the subject, and can all be completed by a student "working five hours per week" (presumably during one academic year).

Following the systematic course, comes a special part for advanced students (140 pages), 50 pages of which are devoted to "Qualitative Organic Analysis Required for the Board of Education Examination, Stage II." This portion is inserted for the benefit of students preparing for these particular examinations,

and the authors themselves are not very enthusiastic about it, for they explain that they "are quite sensible of the fact that the analysis of such mixtures cannot be regarded as useful practical organic chemistry." Then come a number of additional preparations, methods for determining vapor density, the ebullioscopic and cryoscopic methods of establishing molecular weights, ultimate analyses, alkaloidal reagents, and so forth.

All illustrations are purposely omitted. The students design their own apparatus, or a model of the apparatus is set up by the instructor. It is no doubt a good plan to encourage beginners to design their own apparatus, but there seems to be no good reason (aside possibly from the slight additional expense) why the apparatus which the assistant is supposed to set up as a model should not be figured.

Reaction equations are likewise left out, the student being expected to look them up for himself.

Too many of the tests appended to the various preparations apply only to the individual compound, and are not in any sense group reactions. In those cases where the chemistry of the change is but imperfectly understood, as with many of the color and pyrogenetic reactions, the educational value of the test is but slight. Such tests are all well enough for analytical purposes, but are rarely of much assistance in understanding the theoretical side of the subject. The fundamental theoretical considerations upon which the preparations and reactions are based should be brought out much more clearly, including fuller explanations of the origin of the various by-products and the way in which they are removed. Greater stress should be laid upon the purification of the crude products. Failure to emphasize this point is apt to encourage careless and slovenly work.

Errors of various kinds are numerous. Incorrect statements are few, mistakes due to careless proof-reading are frequent. In the former category would fall the statement (on page 142) that the action of bromine water upon salicylic acid gives a precipitate of *tribromsalicylic acid*, whereas the product is really tribromphenol bromide. Among the errors due to careless proof-reading are many which are confusing and misleading. There is space here to mention but few of these. On page 32, a solution containing *ethyl* alcohol is oxidized and the oxidation product tested for *formic* acid. On page 182, in the preparation of ethyl nitrate, a

misplaced comma is responsible for the statement that "when nitric acid alone is used, the acid oxidizes, some of the alcohol being itself reduced to nitrous acid." On page 184, *ev*olution appears instead of *s*olution. On page 194, in describing the preparation of quinoline, the student is told that, after the first stage of the reaction has been induced by gentle warming, "the flame must then be *renewed*." Such a misprint may lead to serious results, as this reaction is one which often proceeds with explosive violence even when the flame is *removed*. On page 196, in describing the synthesis of succinic acid, a wandering semicolon causes it to appear that "ethylene dibromide is boiled with potassium cyanide, and ethylene dicyanide is formed on hydrolysis." On page 218, line 5 from the top, the omission of "not" completely reverses what the authors intended to say. In other cases, the language is anything but clear. Take, for example, the following test for albumin (page 204): "Strong nitric acid yields a white precipitate, which on boiling becomes yellow, and after cooling the addition of ammonia becomes darker (orange)."

The selection of preparations is also open to criticism. The preparation and handling of hydrogen cyanide, for example, is too dangerous for any but experienced hands. A disproportionate amount of space is allotted to the alkaloids.

The book is evidently prepared mainly for the chemical students in the Manchester Municipal School of Technology, to be used only under the supervision of the demonstrator, to whom the student is constantly referred for further information and advice, and without whose assistance the book would be of but little service.

It is printed on one side of the paper only, so that the actual number of pages of text is but half that given. The blank side of the page is for the student to record reactions, observations, and so forth; but, as he is supposed to keep a note-book also, the need of the blank pages is not obvious. The size of the volume is further increased by the inclusion of a 48-page list of books for sale by the publishers.

The book contains many good features and, with the changes above suggested, should prove useful.

MARSTON TAYLOR BOGERT.

RECENT PUBLICATIONS.

LABORATORY MANUAL OF CHEMISTRY FOR SECONDARY SCHOOLS. By N. A. Morse. New York: Appleton & Co. 1905. 3+163 pp. 60 cents.

TRAITÉ D'ANALYSE CHIMIQUE QUALITATIVE. By R. Fresenius Paris: Masson & Cie. 6+769 pp. 7 fr.

GLUE, GELATINE, AND THEIR ALLIED PRODUCTS. PRACTICAL HANDBOOK FOR MANUFACTURER, AGRICULTURIST AND STUDENT OF TECHNOLOGY. By T. Lambert. London: Griffin. 1905. 166 pp. 5/.

GRUNDBEGRIFFE DER HÖHEREN MATHEMATIK FÜR CHEMIKER. By Kurt Arndt. Berlin: Mayer & Müller. 1905. 60 pp. M. 1.50.

GUIDE PRATIQUE DE CHIMIE: 2e PARTIE, CHIMIE ORGANIQUE. By L. Boucherie and E. Coudray. Paris: Rousset. 1454 pp. 15 fr.

CHEMISTRY PAPERS (Matriculation). From June 1875 to September 1905. London: Clive. 1905. 94 pp. 1/6.

QUALITATIVE CHEMICAL ANALYSIS, ORGANIC AND INORGANIC. By F. Mollwo-Perkin. Second Edition. London: Longmans, Green & Co. 1905. 316 pp. 4/.

ZUR KENNTNISS DER DERIVATE AROMATISCHER KETONE UND ALDEHYDE MIT MEHRWERTIGEN JOD. DISSERTATION. By Hans Bogel. Freiberg i/B: Speyer & Kaerner. 1905. 38 pp. M. 80.

ZUR KENNTNISS DES *o*-TOLYLALDEHYDS. DISSERTATION. By Glieb. Daemisch. Freiberg: Speyer & Kaerner. 1905. 34 pp. M. 1.20.

DIE ANALYTISCHE BESTIMMUNG V. ZINN UND ANTIMON. By Laurent Parry. Leipzig: Veit & Co. 1906. 78 pp. M. 2.

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A CORRECTION.

The title of the article on page 104 of the January number should be "The Action of Pyridine on Salicyl Chlorides," instead of "The Action of Pyrimidine on Salicyl Chlorides."